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IN ALL ITS APPLICATIONS TO

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# THE CHEMICAL NEWS.

VOLUME LXVII.

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No. 1728.—JANUARY 6, 1893.

## ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANIDES.

By J. H. GLADSTONE, D.Sc., F.R.S.

In the Chemical News for October appear the four parts of a paper by Mr. H. M. Vernon on "The Reactions of Ferric Salts with Sulphocyanides." He begins by referring to my experiments published in the *Phil. Trans.* of 1855, p. 179, which he says were made "with a view to determining whether the quantity of a salt formed in a solution was dependent on the masses of the reacting salts in accordance with the law of mass action, the importance of which was then only beginning to be thoroughly recognised." He further states: "The results obtained did not appear to obey the law of mass."

Now, the object of my paper was, as its title imports, to examine the "circumstances modifying the action of chemical affinity." I sought, in fact, to decide by crucial experiments between the then contending theories of Bergman and Berthollet; and the influence of mass was merely one of the points studied with this view. The changes of amount of a coloured salt by varying the mass of one of the colourless salts in the solution had a very important bearing on the question of reciprocal decomposition; but of course I was unacquainted with the mathematical law of mass, which was not discovered till many years afterwards by other observers.

Mr. Vernon has also apparently misunderstood my ferric sulphocyanide experiments themselves, as well as the conclusions I drew from them nearly forty years ago. On the appearance of the first instalment of his paper, I wrote to him, pointing this out. He replied expressing his regret, but in subsequent papers no correction has appeared, so I am compelled to make the correction myself. In doing so, I propose to examine his experiments and point out where they differ from, corroborate, or supplement my own.

In the first place, it is only due to Mr. Vernon to state that his investigation contains a very large amount of work, which has evidently been carefully performed; and that he has described various reactions which, as far as I know, have never been observed before. My objection is not to his experimental results, which are never in direct contradiction to my own, but to the very theoretical conclusions drawn from them.

Mr. Vernon attributes much to his method of determining the amount of ferric sulphocyanide formed, and says it differs essentially from mine. It does so; but I was acquainted with both methods. On turning to the appendix to my paper (note B, p. 222) it will be seen that after the presentation of the paper, and to meet a question suggested by Prof. Stokes, I did make experiments in the way Mr. Vernon has adopted. On turning to Note A, p. 221, there will be found reasons for preferring the method I employed. I believed then that the horizontal method would give the truest results. I believe so still.

Mr. Vernon says that I assumed that the water added had no reducing effect on the colour of the ferric sulphocyanide beyond that due to dilution. So far from this being the case, it was well known to me, and was studied at considerable length, as will be seen at pp. 201 to 203, and p. 222. It was subsequently worked out numerically by me. (See *Quarterly Journal of the Chemical Society* for 1858, p. 36).

### *Effect of Increased Mass.*

The experiments described in the Chemical News, vol. lxvi., p. 178, and the accompanying diagram, corroborate the statements of my paper in two points:—

1. That to a given dilution of a mixture of equivalent quantities of ferric salt and a sulphocyanide, the addition of further quantities of ferric salt increases the amount of ferric sulphocyanide more and more.

2. That if water be added to a mixture of ferric salt and sulphocyanide a "reduction of colour effect ensues," over and above what is due to the greater bulk of the solution.

The curves in my paper, and those in Mr. Vernon's diagram on p. 178, represent totally different phenomena. My curves always represent the increasing amount of ferric sulphocyanide produced when the proportion of one of the two salts mixed together is increased. Mr. Vernon's, on the contrary, represent the effect of different amounts of water on the ferric sulphocyanide in the several mixtures. It is this action which, he says, confirms the "law of mass." It may be so; but I cannot admit the different values which he attaches to A (the colour value at infinite concentration), in the table on p. 179, excepting that in the first column, 1 : 100, where the extrapolation is not carried very far. Whatever may be the case at infinite concentration, it is evident from Mr. Vernon's table that at any dilution, such as 400 litres, it is the 1 : 1 solution that has the least colour effect, due to ferric sulphocyanide, and 1 : 100 that has the most.

The assumption "that ferric chloride and potassic sulphocyanide in equivalent quantities react almost completely at infinite concentration to form ferric sulphocyanide," seems to depend upon an experiment in which he prepared such a mixture and compared it with a solution of ferric sulphocyanide, which was prepared by decomposing barium sulphocyanide by ferric sulphate. He found them to be very nearly alike in colour value.

Of course, the observation was not made at infinite concentration, or anywhere near it, but as it came into direct collision with my own view, that in such a mixture there would only be formed about 17 per cent of the possible ferric sulphocyanide, I sought for the cause of the discrepancy. It was not far to seek. In the original investigation I endeavoured to make ferric sulphocyanide by the same process, but I state that it is always impure, containing some ferrous salt and free sulphur. However, I asked Mr. Hibbert to repeat Mr. Vernon's experiment. He obtained the same result as Mr. Vernon, an approximate similarity in the depth of red colour in the two solutions; but at the same time he verified my old statement that ferric sulphocyanide so produced was very impure, and found that so far from the solution containing the theoretical quantity of ferric sulphocyanide, the red colour was greatly increased by the addition of more of either ferric chloride or potassic sulphocyanide.

There is, therefore, no reason to suppose that in a mixture of equivalent amounts of ferric chloride and potassium sulphocyanide the ordinary law of reciprocal decomposition and the usual effect of increased mass do not hold good.

### *Influence of the Other Radicals Present in Determining the Amount of Ferric Sulphocyanide.*

In the Chemical News, vol. lxvi., pp. 191 and 202, Mr. Vernon describes a large number of experiments in which he mixed different ferric salts with different sulphocyanides, and that at different degrees of dilution. His results, as exhibited in the table on p. 192, are perfectly in accordance with my general views; in several respects they confirm my experiments, and in others go beyond them. They show:—

1. That the amount of red salt produced is affected by the *nature* of every other substance that is present in the solution.

2. That it is affected by the *mass* of the different substances present.

The amount produced where 100 equivalents of ferric salt are employed is invariably far greater than when the proportion is that of single equivalents. We are able to compare the mixture of equivalents of sulphocyanide of potassium with 1 and with 100 equivalents of ferric chloride at a dilution of 160 litres. They are as 18·6 to 163·4; that is, the mixture which contains a very large excess of ferric chloride gives nearly nine times as much indication of the red salt as the other one does. This difference is no doubt exaggerated by two circumstances, the effect of water being greater on the dilute than on the strong sulphocyanide solution, and the excess of undecomposed ferric chloride being itself red in colour. Still, after making due allowance for these qualifications, the results are fully confirmatory of my views on the influence of mass.

3. That the order in which the different ferric salts are decomposed by the sulphocyanide is the same as in my paper, and the proportions are nearly the same.

The following table gives the colour value of a mixture of equal equivalents of the given ferric salt and potassium sulphocyanide:—

| Ferric Salt. | Colour Value. | |
|---|---|---|
| | Vernon. | Gladstone. |
| Nitrate .. .. | 10·4 | 10·0 |
| Chloride . .. | 9·0 | 8·9 |
| Sulphate . .. | 7·5 | 6·5 |
| Acetate .. .. | 1·7 | 2·0 |

I obtained a still smaller colour value from the citrate than Mr. Vernon did, and I give no quantitative values as derived from the tartrate.

4. That the nature of the base originally combined with sulphocyanogen has a great influence on the results.

I proved this, but did not work it out quantitatively, except once in the case of hydrogen. Mr. Vernon gives actual figures. From his table we learn that the order in which the colourless sulphocyanides are decomposed is: potassium most easily, then ammonium, sodium, calcium, and barium. We learn also that this is the case whether we are dealing with 100 equivalents of ferric salt or equal equivalents.

5. Another important matter which may be deduced from Mr. Vernon's figures is, that, for producing the coloured salt, the order of the bases is practically the same whatever may be the acid radical of the ferric salt, and the order of the acids is the same whatever may be the base of the sulphocyanide; and that this is true for both the degrees of dilution given.

### *Effect of Changes of Temperature.*

There is a series of experiments in the Chemical News, vol. lxvi., p. 214, on the effect of variation of temperature upon different solutions containing ferric sulphocyanide. The changes of colour are very marked. They are not of a permanent nature, for the original degree of colour is restored on cooling. The experiments are new and interesting, but Mr. Vernon has been led astray in the explanation of them, through his having omitted to notice the effect of temperature on the excess of ferric salt not sulphocyanide. Thus, in the first six experiments, he took 100 equivalents of ferric chloride mixed with 1 equivalent of the colourless sulphocyanides of potassium, ammonium, sodium, lithium, barium, and calcium; and on heating them from 20° to 60° C., the colour was increased in each instance about 40 per cent. It is evident that each solution must have had at least 99 per cent of its iron in the condition of undecomposed ferric chloride, and, as this is itself a reddish salt, the colour of the solution must have been partially due to it. Now, on referring to my paper "On the Effect of Heat on the Colour of Salts in Solution" (*Phil. Mag.*, December, 1857), it appears that on heating its solution "sesquichloride of iron passes from orange to a deep and almost pure red."

No figures were there given, so I have thought it worth while to look into the matter a little further. It was found on experiment that not only does the ferric chloride change colour on heating, but the amount of change varies greatly with the proportion of water present and the length of time during which the heating is continued. Thus in a 3·8 per cent solution the depth of colour was about doubled at once when heated from 20° to 60° C.; while in a 0·06 per cent solution it increased fourfold. These figures are inevitably vague on account of the change of tint. It was found also that the colour of a solution containing 100 equivalents of ferric chloride at the ordinary temperature is increased about twenty-fold on the addition of 1 equivalent of potassium sulphocyanide; but when the two are compared at 60° the increase is not nearly so great.

This suggested the idea that the effect of rise of temperature on the ferric sulphocyanide might actually decrease its colour value. That this is the case is pretty evident from Mr. Vernon's observations that the actual value of a mixture of single equivalents of ferric chloride and potassium sulphocyanide (where, of course, very nearly all the colour was due to the deep red ferric sulphocyanide), was, on heating, reduced from 100 to 46·8. But the matter was tested further by heating a solution of the impure ferric sulphocyanide, obtained by the double decomposition of ferric sulphate and barium sulphocyanide. This was also weakened in colour on heating; but a better experiment was made by mixing 1 equivalent of ferric chloride with 100 equivalents of potassium sulphocyanide, when, according to the laws of reciprocal decomposition, very little undecomposed ferric chloride could have been in the solution. The colour value of the deep red salt was diminished 50 per cent on heating from 20° to 60° C.

This result, if true, is curious, as it indicates that the action of increased temperature on ferric sulphocyanide is analogous to that of increased dilution, while in all solutions of coloured salts examined by me in 1857, I found "the increase of heat having the opposite effect to an addition of water." It is possible, however, that this reduction may be brought about by a change in the relative affinities arising from the change of temperature.

Without discussing Mr. Vernon's theoretical conclusions, it therefore appears to me that the whole of his careful experiments not only are in accordance with my old views of the reciprocal decomposition of salts in solution, but furnish some additional arguments in their favour.

## ON THE ABSORPTION OF NITROGEN BY PLANTS.*

By GEORGES VILLE.

WHEN I began my experiments on the absorption of nitrogen by plants the reigning opinion attributed all the nitrogen of plants over and above that of the manures to the ammonia of the air.

The first point to solve was, therefore, to know if the air really contained ammonia, and if this ammonia occurred there in a quantity sufficient for the great part ascribed to it.

I will not again return to my determinations of ammonia, which you know; I confine myself to remind you that I devoted to this research two entire years, and that the result of sixteen determinations was, as a mean, in 100 cubic metres of air, 2·84 m.grms. Ten years later, M. Schlœsing found 2·56; difference, 0·28 milligrm. referred, in round numbers, to 130 kilogrms. of air.

2. At the side of the apparatus which served for the determination of the ammonia there was a second apparatus consisting essentially of a glass bell in connection with a second aspirator, which conveyed into the interior of the bell a volume of air approximately equal to that which served for the determination of the ammonia in an independant apparatus placed at its side.

The following was the result of the experiment:—

| | | |
|---|---|---|
| Nitrogen of the crop.. .. .. .. .. .. .. | | 0·258 grm. |
| Nitrogen of the ammonia of the air .. .. .. .. | 0·001 grm. } | .. 0·155 „ |
| Nitrogen of the seed .. | 0·154 „ } | |
| Nitrogen absorbed by the plants .. .. .. .. | | 0·103 „ |

This experiment having been contested, I offered the Academy to repeat it under a commission which it should nominate. My offer was accepted. This commission, consisting of MM. Chevreul, Dumas, Payen, Regnault, Péligot, drew up the programme which I was to follow, to which I submitted without discussion.

The experiment executed at the museum consisted, in fact, of two independent experiments: the first, where the plants, cultivated in calcined sand, were shut up in a cage of metal with glass sides; the second, executed under a small glass bell, was in reality the exact copy of my former experiment of 1849.

We will first take the result of the experiment performed in the metal cage. The plant selected was cress:—

| | Weight of crop. Grm. | Weight of seed. Grm. | Proportion of crop to seed. | Excess of nitrogen in crop. Grm. |
|---|---|---|---|---|
| No. 1. | 2·241 | 0·319 | 7 times | 0·000 |
| No. 2. | 1·506 | 0·127 | 11 „ | 0·007 |
| No. 3. | 5·021 | 0·124 | 48 „ | 0·050 |

We see that the experiment consisted of three independent cultivations in separate pots, all three plunged in the same basin of distilled water.

*Nitrogen.*

| | In crop. Grm. | In seed. Grm. | Proportion of nitrogen in the crop to that in seed. | Nitrogen drawn from the air. Grm. |
|---|---|---|---|---|
| No. 1. | 0·0097 | 0·0099 | Equal | 0·000 |
| No. 2. | 0·011 | 0·0039 | 2·9 | 0·007 |
| No. 3. | 0·053 | 0·0038 | 13·9 | 0·050 |

From reasons which it is needless to recal, the commission decided that a second experiment subsidiary to the former should be made. To this end, a small glass bell was fixed, in which there should be only a single cultivation of cress in calcined sand, the air of the metal cage passing into the small bell before entering the aspirator. This was, in fact, making separate experiments with the same air. The following was the result of the second experiment:—

*Experiment of* 1853 *on Cress.*

| | |
|---|---|
| Weight of crop .. .. .. .. | 3·60 grm. |
| Weight of seed .. .. .. .. | 0·206 „ |
| Proportion of crop to seed .. .. | 17·4 |

*Nitrogen.*

| | |
|---|---|
| In crop .. .. .. .. .. .. | { 0·0035 grm.<br>0·035 „ |
| In seed .. .. .. .. .. .. | { 0·0063 „<br>0·0063 „ |
| Proportion of N in crop to that of seed .. .. .. .. .. .. | 5·5 |
| N drawn from air .. .. .. .. | 0·0287 grm. |

The second experiment concluded like the former. I consider it the purest and most irreproachable that has ever been performed, considering that there were employed only 500 grms. calcined sand and a litre of distilled water, which scarcely contained 0·0001 of nitrogen!

But what gives it for me an inestimable value is that it reproduces, term for term, my experiment of 1849 in a limit of approximation of which, to my knowledge, the history of vegetable physiology offers no instance.

Permit me to introduce here my experiment of 1849, as I have given that of 1853, to render the comparison easier and more striking:—

| | |
|---|---|
| Weight of crop .. .. .. .. | 8·13 grm. |
| Weight of seed .. .. .. .. | 0·531 „ |
| Proportion of crop to seed .. .. | 16·6 „ |

*Nitrogen.*

| | |
|---|---|
| In crop .. .. .. .. .. .. | 0·147 grm. |
| In seed .. .. .. .. .. .. | 0·026 „ |
| Proportion of N in crop to that of seed .. .. .. .. .. .. | 5·6 |
| N derived from air .. .. .. .. | 0·108 „ |

Finally, these are the experiments which M. Bréal, the assistant of M. Dehérain, has just verified, placing himself, in my opinion, in conditions much less rigorous than those in which I operated.

The year 1853 was one of the most harassing of my life. When I asked the commission for a locality for the experiment of control, I was shown, in Rue Paliveau, at the extremity of the nursery grounds of the museum, a vague plot where there was neither a house, nor buildings, nor water. I had to construct everything: a shelter for my aspirator—a shed, the walls and the roof of which were bitumenised paper. To work my aspirator, I had to construct an artificial reservoir. I was then living at the opposite extremity of Paris, in the suburb of Grenelle, at a distance of 8 kilometres from the museum, which I had to traverse twice daily.

In an early letter I will explain to you three demonstrations of the absorption of nitrogen of a different character which I have produced. This I can do the

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* Extracts from a letter to the Editor.

more easily, as the library of the Royal Society contains my "Recherches Experimentales," edition in 4to., of 1853, and the more complete 8vo. edition of 1868.

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## SOME RESULTS AND CONCLUSIONS DERIVED FROM A PHOTOGRAPHIC STUDY OF THE SUN.

By GEORGE E. HALE.

In view of the fact that the study of prominence, facula, and sun-spot spectra by photographic means has now been taken up by several investigators, it seems desirable to bring together the results of the work in this direction which has been in progress at the Kenwood Observatory since April, 1891. Some of these results have been published before or casually referred to in papers on other branches of solar work, but they cannot fail to be of greater value for comparison with the investigations of others if grouped in a single article. There also remain to be mentioned several disconnected matters to which attention has not yet been called.

The following are some of the results, with several conclusions to which I have been led; further investigations may very possibly render necessary material modifications in the views here expressed.

### *Chromosphere and Prominences.*

1. H and K are always present as the strongest lines in the chromosphere and prominence spectrum.

2. These lines extend to the highest parts of all prominences, but have not yet been traced to any greater distance from the limb, *i.e.*, into the corona.

3. K seems to be invariably stronger than H, and extends farther from the limb.

4. In cases of motion in the line of sight the distorted forms of the H and K lines are similar.

5. Prominences have the same form in both lines. Where apparent differences exist they may probably be ascribed to the greater brightness of K. (This remark also applies to 4).

6. Both H and K expand rapidly in width from the upper surface of the chromosphere to its base. Consequently photographs taken with the slit just tangent to the limb show these lines more than twice as broad as they appear in the higher regions of prominences.

7. Both lines are often doubly reversed (narrow dark lines running down the centre of the bright lines) in the chromosphere, and sometimes in the base of bright prominences.

8. H is always accompanied by a hydrogen line (H$\epsilon$), but this line is much fainter, and does not extend so high in prominences.

9. The entire series of ultra-violet hydrogen lines have been photographed in very bright prominences, but in faint prominences the lines more refrangible than $\alpha_1$ or $\beta_1$ are usually absent from the photographs. They may, however, be present as very faint lines in all prominences, but remain invisible on the photographs on account of the brilliancy of the atmospheric spectrum.

10. The line $\alpha_1$ is frequently accompanied by a line slightly more refrangible, which is probably not due to hydrogen. In a few cases $\alpha_1$ has been single in certain parts of a prominence, and double in other parts.

11. The upper component of $\alpha_1$ is sometimes doubly reversed in the chromosphere.

12. No prominence has yet been found which showed the H and K lines alone, *i.e.*, without some of the less refrangible hydrogen lines.

13. The forms of prominences as observed in C and in H and K seem to be the same, though they may be more extensive in the latter lines.

14. Prominences seem to have the same motion in the line of sight, whether observed in C or in H and K. (In one case where the motion of the entire prominence was considerable, a large number of lines in the ultra-violet, all that were visible on the photograph, were equally displaced with H and K).

15. The spectra of eruptive prominences frequently contain many metallic lines in the ultra-violet; notably the magnesium triplet at $\lambda 383$. (See my article on "The Ultra-Violet Spectrum of the Solar Prominences").

16. Eruptive prominences sometimes exhibit a continuous spectrum in the ultra-violet.

17. Prominences frequently show evidences of spiral motion.

### *Faculæ.*

18. Both H and K are always reversed in faculæ.

19. These reversals are usually (if not invariably) double, a narrow dark line running down the centre of the broader bright line. The appearance on the photograph is consequently as if there were two narrow bright lines separated by a narrow dark line, in the centres of the broad dark shades at H and K. In some instances I have noticed that one of these narrow bright lines was missing in certain portions of a facula, an unsymmetrical double reversal resulting.

20. Distortions in the doubly reversed H and K lines of the faculæ are rare. I have found but one or two instances of this kind, and in these cases the distortions took the form of expansions in the lines.

21. H is usually unaccompanied by the slightly less refrangible hydrogen line, referred to above as being always present in prominences. In a few cases, however, this line has been found extending across spots, and for some distance in the faculæ on either side.

22. Neither $\alpha_1$ nor any other bright lines more refrangible than H and K have been found in faculæ or spots.

23. Curved forms predominate in faculæ, and suggest some relation with spiral forms in prominences.

### *Spots.*

24. The bright H and K lines seem to invariably extend entirely across every sun-spot. Both lines are doubly reversed in the faculæ which probably completely surround every spot. In the umbra the reversals are narrower, and the dark central line is usually absent.

25. Small spots, especially when members of a group containing large spots, are frequently completely covered with faculæ.

26. In the ultra-violet spectra of spots the dark lines of the solar spectrum do not seem to undergo selective widening, as in the less refrangible parts of the spectrum. Beyond the presence of the bright H and K lines, and the infrequent appearance of H$\epsilon$, the spot spectrum seems to differ from the ordinary solar spectrum only by the increased general absorption.

27. Distorsions of the bright H and K lines in spots are extremely rare.

### *Conclusions.*

28. The exact agreement of H and K with the two strongest lines in the spectrum of the calcium spark leads me to attribute these prominence lines to calcium. While the properties of calcium in its terrestial condition make it difficult to see how its vapour can form the most important constituent of the prominences, yet I do not see how we are to escape from this conclusion.

29. No other than a negative conclusion can as yet be offered in regard to the perplexing question of the so-called "white prominences." At the eclipse of August 29, 1886, a large prominence was photographed which was said by Professor W. H. Pickering to have no other lines in its spectrum than H and K, and a faint trace of an ultra-violet line, in addition to a bright continuous spectrum. He goes on to add (*Annals of Harvard College Observatory*, vol. xviii., No. 5, p. 100): "It was therefore quite invisible, both before and after totality, by the usual spectroscopic method, as was in fact noted at the time by

Professor Tacchini." The character of the photograph, at least so far as can be judged from the reproduction accompanying the report, was hardly such as to warrant any very positive statement as to the absence of the hydrogen lines, particularly as they might have been partly obscured by the bright continuous spectrum. The prominence might also have been eruptive in nature, not lasting longer than the duration of totality, and thus may not have existed when Professor Tacchini made his observations before and after the eclipse. However, this may be, for this is only one of a number of cases in which "white prominences" have been recorded, I have as yet found no prominences which exhibited H and K without the hydrogen lines. This point has not been made the subject of special investigation, however, and it may be that some cases of the kind may ultimately be brought to light.

30. The fact that small spots are sometimes completely covered with faculous matter (or possibly with prominences) may assist in explaining the anomalous heat radiations recently measured in certain spots by Professor Frost (*Astronomy and Astro-Physics*, October, 1892). I hope to take up this point more in detail elsewhere.

31. Photographic methods have abundantly substantiated the conclusions long ago drawn from visual observations in regard to the nature of faculæ. In a great many photographs taken with the spectroheliograph, faculæ are shown projecting above the sun's limb. And the intimate relationship between faculæ and eruptive prominences is not less evident, especially in composite photographs showing faculæ and prominences on the same plate. When we consider that eruptive prominences probably arise from faculæ, it is not at all surprising that such prominences sometimes show a continuous spectrum in addition to their bright lines. For a violent eruption would naturally carry up with the prominence some "dust-like" (See Fényi, *Astronomy and Astro-Physics*, May, 1892, p. 431) matter from the faculæ, which would give a continuous spectrum.

32. The reversals of the H and K lines over spots seem to be readily explainable. As has been stated above, the reversals are double in the penumbra, and also for a considerable distance on either side of the spot, but usually single in the umbra. As spots seem to be always surrounded by faculæ, which frequently encroach upon the penumbra, the double reversals occur in these just as they do in faculæ not in the vicinity of spots. The single reversals in the umbra, however, probably take their rise in the chromosphere, which presumably overlies the cooler regions of the spot.—*Astronomy and Astro-Physics*, No. 109.

## REPORT ON THE TECHNICAL DETERMINATION OF ZINC.*

In accordance with the plan outlined some time since, your committee appointed for the purpose has undertaken the work of attempting to establish a uniformity in the technical methods of analyses in the West, and as the result of its first effort it herewith presents to your body the work of a number of our best known western chemists on zinc determination.

It may be remarked that the samples of ore on which the work was done were such as seemed to offer the greatest difficulty in the correct determination of the metal in question.

The ores so submitted were from a number af mines of widely separated localities; they were mixtures of galenite, pyrite, and sphalerite, accompanied by greater or less percentages of manganese in the form of rhodochrosite, associated with a quartzose gangue.

That a standard of comparison might be had by which the various results could be judged, the assistance of the chemical laboratory of the U.S. Geological Survey at Washington, D.C., was invoked. Mr. F. W. Clarke, Chief Chemist of the Survey, notwithstanding the fact that his department is always busily engaged with work correlated to the geological investigation of the survey, met our request for the co-operation of his laboratory in the work to be undertaken with the greatest willingness, and your committee takes this occasion to express its deep appreciation of the valued assistance thus afforded.

The analyses were made by Mr. L. G. Eakins, one of the ablest of Mr. Clarke's corps of chemists, and your committee does not doubt that the results furnished by him will unhesitatingly be accepted as standard by all the technical chemists who assisted in the investigations.

The samples of ore distributed came from the following mines:

Enterprise Mine, at Rico, Colorado.
Mary Murphy Mine, near St. Elmo, Colorado.
Robinson Mine, Robinson, Colorado.
New York Mine, near Park, Colorado.
Moyer Mine, Leadville, Colorado,—the ore from this property being a concentrate product.

These were designated, respectively, Nos. 5, 9, 11, 13, and 20, great care being taken in the mixing of each separate large sample, so that uniformity in the material subsequently distributed might be assured.

The analytical methods employed by the different chemists are given, together with the results obtained. In one instance, that of Dr. H. C. Hahn, in conjunction with the zinc determination, that of manganese is also furnished, thus happily affording a knowledge of the extent to which the latter element was present.

*Method of L. G. Eakins, Chemist U.S. Geological Survey, Washington, D.C.*—About one grm. of ore was treated with twenty-five c.c. of dilute hydrochloric acid (1 : 1) and after digestion on the water bath three c.c. of nitrate acid were added, the whole being then evaporated to dryness. The dried mass was digested with dilute hydrochloric acid and water, and the insoluble residue filtered off. The filtrate was precipitated with hydrogen sulphide, filtered, and the precipitate re-dissolved in nitrohydrochloric acid, evaporated nearly to dryness, and water and hydrochloric acid added.

This solution was once more precipitated with hydrogen sulphide, the precipitate filtered off, washed, and the filtrate combined with the first. The solution was now oxidised with nitric acid, and a basic acetate precipitation made. The resulting precipitate was filtered off, dissolved in dilute hydrochloric acid, and re-precipitated as basic acetate, filtered, and this precipitate again dissolved. This solution was evaporated to expel excess of acid, and then poured with constant stirring into an excess of strong, cold ammonia, the precipitate allowed to stand for some time, after which it was filtered off and washed.

The solution from the last ammonia precipitation was found in every case to still contain zinc which had not been removed by the two previous basic acetate precipitations, the amount so held varying from 0·30 per cent. to 2 per cent.

The filtrates from the basic acetate precipitations were combined, evaporated to a convenient bulk, about 5 grms. of acetate of sodium and five c.c. of glacial acetic acid added, the solution heated to boiling, and the zinc precipitated with hydrogen sulphide. The precipitated sulphide was allowed to settle, the solution filtered, and the precipitate washed with hydrogen sulphide water containing acetate of sodium.

The filtrate obtained from the ammonia precipitate was now evaporated to expel excess of ammonia, acetate of sodium and glacial acetic acid added, and the zinc precipitated as sulphide in the same way as has just been described.

The zinc sulphide precipitates were combined and digested with dilute hydrochloric acid containing hydro-

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* A report read at a meeting of the Colorado Scientific Society.

gen sulphide. All arsenic and traces of nickel (if present) were left undissolved, the zinc and any cadmium that might be present passing into solution. This solution was filtered, the filtrate evaporated to expel the hydrogen sulphide, and the zinc precipitated as carbonate with carbonate of sodium in the usual way, being finally weighed as oxide of zinc.

This was dissolved in dilute hydrochloric acid, the small amount of silica which may have contaminated the precipite filtered off, washed, and weighed.

To the filtrate an excess of tartaric acid was added, then an excess of caustic soda, and after the solution was diluted to a large bulk it was boiled in a platinum dish to precipitate any cadmium which might have been associated with the oxide of zinc. The precipitate so obtained was filtered off, washed, and weighed, and correction made for such amount, together with what silica had previously been found.

The result were as follows:

| | |
|---|---|
| No. 5 | 14·64 per cent. zinc. |
| ,, 9 | 24·11 ,, ,, ,, |
| ,, 11 | 10·71 ,, ,, ,, |
| ,, 13 | 6·31 ,, ,, ,, |
| ,, 20 | 16·09 ,, ,, ,, |

Note: Sample number five contained appreciable quantities of cadmium, sample number nine very small quantities, and the other samples only traces of this element.

*Method of Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado.*—Prepare a solution of ferrocyanide of potassium by dissolving 44 grms. of pure salt in distilled water and diluting to one litre. Standardise as follows:—

Dissolve exactly 200 m.grms. of pure oxide of zinc in a beaker in ten c.c. of strong pure hydrochloric acid. Now add 7 grms. of C. P. chloride of ammonium (the commercial article frequently contains a little copper), and about a hundred c.c. of boiling hot water. Titrate the clear liquid with the ferrocyanide solution until a drop, when tested on a porcelain plate with a drop of a strong aqueous solution of acetate of uranium, shows a brown tinge. About sixteen c.c. of ferrocyanide will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing afrer each additional drop of ferrocyanide. As soon as a brown tinge is obtained note the reading of the burette, and then wait a minute or two and observe if one or more of the previous tests do not also develop a brown tinge. Usually the end-point will be found to have been passed by a test or two, and the proper correction must then be applied to the burette reading. Finally make a further deduction from the burette reading of the amount of ferrocyanide required to produce a brown tinge under the same conditions when no zinc is present. This correction is about two drops, or 0·14 c.c.

200 m.grms. of oxide of zinc contain 160·4 m.grms. of zinc, and one c.c. of the above standardised solution will equal about 0·01 grm. of zinc, or about 1 per cent. when 1 grm. of ore is taken for assay.

Prepare the following solutions for the essay of ores:—

A saturated solution of chlorate of potassium in nitric acid, made by shaking an excess of the crystals with the strong pure acid in a flask. Keep the solution in an open flask.

A dilute solution of chloride of ammonium containing about 10 grms. to the litre. For use heat to boiling in a wash bottle.

A wash bottle of hot water.

Take exactly 1 grm. of the ore and treat in a 3½ inch casserole with twenty-five c.c. of the above chlorate solution. Do not cover the casserole at first, but warm gently until any violent action is over and greenish vapours have ceased to come off. Then cover with a watch-glass and boil rapidly to complete dryness, but avoid over-heating and baking. A drop of nitric acid adhering to the cover does no harm. Cool sufficiently and add 7 grms. of chloride of ammonium, fifteen c.c. of strong ammonia water, and twenty-five c.c. of hot water. Boil the covered mixture one minute, and then, with a rubber-tipped glass rod, see that all solid matter on the cover, sides, and bottom of casserole is either dissolved or disintegrated. Filter into a beaker and wash several times with the hot chloride of ammonium solution. A blue-coloured filtrate indicates the presence of copper. In that case add twenty-five c.c. of strong pure hydrochloric acid and about 40 grms. of granulated test-lead. Stir the lead about in the beaker until the liquid has become perfectly colourless and then a little longer to make sure that the copper is all precipitated. The solution, which should still be quite hot, is now ready for titration. In the absence of copper the lead is omitted and only the acid added. About one-third of the solution is now set aside, and the main portion is titrated rapidly with the ferrocyanide until the end-point is passed, using the uranium indicator as in the standardisation. The greater part of the reserved portion is now added, and the titration continued with more caution until the end-point is again passed. Then add the remainder of the reserved portion and finish the titration carefully, ordinarily by additions of two drops of ferrocyanide at a time. Make corrections of the final reading of the burette precisely as in the standardisation.

Gold, silver, lead, copper, iron, manganese, and the ordinary constituents of ores do not interfere with the above scheme. Cadmium behaves like zinc. When known to be present it may be removed, together with the copper, by the proper treatment with hydrogen sulphide, and the titration for zinc may be made upon the properly acidified filtrate without the removal of the excess of gas. There seems to be no simpler way to remove cadmium.

The following results were obtained on the samples of ore sent us by the Colorado Scientific Society. Each sample was assayed only once. The weighing was done on the ordinary ore-scale and the burette used had not been corrected. It was intended to show just what would be obtained by the method in ordinary technical work.

| | |
|---|---|
| Sample No. 5 | 15·31 per cent. zinc. |
| ,, ,, 9 | 24·34 ,, ,, ,, |
| ,, ,, 11 | 10·76 ,, ,, ,, |
| ,, ,, 13 | 6·42 ,, ,, ,, |
| ,, ,, 20 | 16·14 ,, ,, ,, |

Notes on the above scheme:

Acids destroy the delicacy of the uranium test, and for this reason a strong aqueous solution of uranium acetate is used. By having the zinc solution only faintly acid the production of the brown colour in the end test becomes almost instantaneous and no previous test will develop a colour. Under these conditions, however, lead is apt to seriously interfere, and the excess of acid recommended above is found to be a necessity. When a strong solution of uranium acetate, not acidified, is used as indicator, the error caused by the excess of acid in the zinc solution amounts to only two drops of ferrocyanide, which may be allowed for, and the brown tinge develops so rapidly that the end-point is seldom passed by more than one test.

When an ore contains but little copper, the granulated lead used frequently coheres in lumps that may hold zinc solution. These lumps are most easily broken up after a little of the ferrocyanide has been added. They appear to cause no appreciable error in the work. Of course, lead shot or thin sheet lead may be used if preferred, and it may be cleaned with strong nitric acid and used repeatedly. It seems simpler and more satisfactory, however, to use the granulated lead and throw it away after use.

As regards the effect of nitric acid, it is found that the addition of one c.c. of the strong acid to the boiling hot zinc solution during the standardisation of the ferrocyanide makes no appreciable difference.

*Method of Mr. L. W. W. Jones, Chemist Pueblo Smelting and Refining Company, Pueblo, Colorado.*—The method used was that published some time since by Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado, which consists in effecting a decomposition of the ore by means of concentrated nitric acid saturated with chlorate of potassium, evaporating to dryness, and bringing the zinc into solution by means of water, ammonia water, and chloride of ammonium; heating the solution to boiling, filtering off the insoluble residue, and washing. If the filtrate shows the presence of copper, this metal is precipitated after acidifying the solution with hydrochloric acid by means of granulated lead.

To the hot solution a few grms. of sulphite of sodium are now added to counteract any effects due to the possible present of free chlorine from the action of the hydrochloric acid on any chlorate that might not have been decomposed, and the zinc titrated with a standardised solution of ferrocyanide of potassium, using acetate of uranium as an indicator.

The readings of the burette were corrected by an amount of ferrocyanide necessary to produce a reaction with acetate of uranium in a blank test, the standardisation having been made under like conditions.

The results obtained on the samples submitted were:—

| | | |
|---|---|---|
| No. 5.. .. .. .. | 15·39 | per cent. zinc. |
| " 9.. .. .. .. | 24·53 | " " |
| " 11.. .. .. .. | 10·83 | " " |
| " 13.. .. .. .. | 6·58 | " " |
| " 20.. .. .. .. | 16·46 | " " |

*Method of Mr. E. N. Hawkins, Superintendent Holden Smelting and Refining Company, Leadville, Colorado.*—One grm. of ore is treated in a 3½ inch casserole with five to ten c.c. of concentrated nitric acid, evaporated to dryness on a hot plate and baked for several minutes. After cooling, twenty to thirty c c. of water are added, and about 7 grms. of chloride of ammonium and fifteen c.c. of strong ammonia water.

If the ore is free from manganese proceed as follows:—

Boil for several minutes, filter and wash with warm water, taking the precaution to add a few drops of ammonia water to the first wash water on filter to keep the zinc in solution. It is more convenient to operate in this way than to use ammoniacal wash water.

Neutralise the filtrate with hydrochloric acid, then add an excess of ten c.c. of the acid. If copper is present precipitate it with granulated lead.

The solution is now ready for titration with ferrocyanide of potassium, uranium acetate being used as an indicator.

If manganese is present, after addition of chloride of ammonium and ammonia water as stated above, add to the solution five c.c. of peroxide of hydrogen and boil. The manganese will all be precipitated as the hydrated dioxide together with such iron and alumina as may be present. Filter, using the regular precautions.

Now dissolve the precipitate in a small quantity of hydrochloric acid, dilute with water, add an excess of ammonia water and again five c.c. of peroxide of hydrogen, boil for several minutes, filter and wash, and combine filtrate with the one previously obtained.

The solution is now made acid with an excess of hydrochloric acid, and the titration of the zinc effected, after removal of any copper that may be present, as previously specified.

In ordinary practice it has been found that the amount of zinc which is carried down with the manganese in its first precipitation by means of peroxide of hydrogen, in the ores which carry from 3 to 10 per cent. of that element, is equal to about 5 per cent. of the total quantity of zinc present, although this does and will vary somewhat with different practice and the amounts of reagents employed.

The results obtained were as follows:—

| | | |
|---|---|---|
| No. 5.. .. .. .. | 15·66 | per cent. zinc. |
| " 9.. .. .. .. | 24·23 | " " " |
| " 11.. .. .. .. | 11·88 | " " " |
| " 13.. .. .. .. | 8·73 | " " " |
| " 20.. .. .. .. | 15·86 | " " " |

*Method of Mr. F. C. Knight, F.C.S., Chemist, Boston and Colorado Smelting Company, Argo, Colorado.*—1 grm. of ore is taken and mixed in a 3½ inch casserole with 10 grms. of nitrate of ammonium and ten c.c. of concentrated nitric acid added. The casserole is covered with a watch-glass and the mixture evaporated to complete dryness on a hot plate. The mass usually deflagrates just before becoming completely dry.

After cooling, about twenty c.c. of water and 5 grms. of chloride of ammonium are added.

If manganese is present, of which previous indication will have been afforded, add to the solution five c.c. of peroxide of hydrogen and ten c.c. strong ammonia water, heat to boiling for two or three minutes, filter, and wash with water containing ammonia water.

As the precipitate of iron and manganese carries zinc, it is re-dissolved in a small quantity of hydrochloric acid, water and chloride of ammonium added, then five c c. peroxide of hydrogen and ten c.c. ammonia water as before. Boil, filter, and wash with hot water rendered ammoniacal, and combine the two filtrates. The second precipitation of the iron and manganese practically brings all zinc into solution.

The filtrate should now measure from two hundred and fifty to three hundred c.c. It is slightly acidified with hydrochloric acid, and if copper is present it is precipitated with granulated lead.

To the solution now add an excess of ten c.c. hydrochloric acid and titrate the zinc with a standardised solution of ferrocyanide of potassium, one c.c. of which is equal to about 5 m.grms. or 0·50 per cent. zinc. Acetate of uranium is used as an indicator of final reaction.

As about five to six drops of the ferrocyanide solution will be absorbed in a blank test before the reaction with acetate of uranium manifests itself, due allowance must be made for this error in the standardisation of the solution. It is almost needless to remark that a similar precaution must be observed in taking the reading of the burette in the actual titration of the zinc solution of the ore. Results obtained were as follows:—

| | | |
|---|---|---|
| No. 5.. .. .. .. | 15·08 | per cent. zinc. |
| " 9.. .. .. .. | 23·80 | " " " |
| " 11.. .. .. .. | 10·69 | " " " |
| " 13.. .. .. .. | 6·85 | " " " |
| " 20.. .. .. .. | 15·90 | " " " |

(To be continued).

## CHESTNUT BARK TANNIN.*

By HENRY TRIMBLE.

In the manufacture of chestnut extract the bark and wood are used together, the latter naturally exceeding the former in amount as well as in yield of extract.

It has been thought desirable to determine if there exists any differences in the character of the tannins from these two parts of the tree, and the results of an investigation of that from the wood were published in the *Journal of the Franklin Institute*, cxxxii., p. 303.

The material in this case was obtained from a tree thirty years old, cut in August; the bark was immediately removed, air dried, and powdered.

The total tannin was found to be 7·31 per cent. The wood yielded 7·85 per cent. The other important con-

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* Read at a Meeting of the Chemical Section of the Franklin Institute.

stituents in the bark were found to be in per cent, 1·09 of resin, 3·06 of mucilage, 1·35 of glucose, 10·00 of moisture, 4·71 of ash, and 45·44 of cellulose.

The tannin, as extracted by commercial ether, was much darker in colour than that similarly prepared from the wood, but an equally light coloured product was obtained by first precipitating in fractions with lead acetate, and then further treating the middle and most abundant one with salt and acetic ether. The aqueous solution of this portion, after removal of lead by hydrogen sulphide, when saturated with common salt, separated a dark coloured portion which rose to the top, and was easily removed in one mass after standing twenty-four hours. The remaining light coloured solution was agitated with acetic ether, the latter separated, and, after removal of the solvent under reduced pressure, a light coloured product was obtained. This was then dissolved in water, filtered, and the solvent distilled off under reduced pressure; it was then dissolved in ether, filtered, and again dried in a vacuum at the temperature of a boiling water-bath.

The product was a light, almost white, porous mass of a reddish brown shade, which was completely and readily soluble in water and the other usual solvents, and in all other respects corresponding with the chestnut wood tannin described in the previous paper, as well as with gallotannic acid. It did not give any reaction for glucose, from which compound it was rather more easily purified than the product from the wood.

The average of two closely agreeing combustions gave the following percentages, with which are given those from the tannin of the wood, for comparison.—

| | Chestnut bark tannin. | Chestnut wood tannin. |
|---|---|---|
| C .. .. .. .. | 52·42 | 52·11 |
| H .. .. .. .. | 4·67 | 4·40 |
| O .. .. .. .. | 42·91 | 43·49 |
| | 100·00 | 100·00 |

The conclusions to be drawn from this work are that the tannins from chestnut bark and wood are identical, and although ultimate analyses show high percentages of hydrogen in both, they are believed to be identical with gallo-tannic acid.

In an investigation of the darker tannin precipitated from aqueous solution by salt, the following percentages were obtained:—

| | |
|---|---|
| C .. .. .. .. .. .. | 55·18 |
| H .. .. .. .. .. .. | 4·72 |
| O .. .. .. .. .. .. | 40·10 |
| | 100·00 |

This product was considered to be a mixture of the tannin with its anhydride.

## THE GOOCH CRUCIBLE.

By TH. PAUL.

The author considers it useful to give as a supplement to the original memoir (Chemical News, xxxvii., 181) a process which has been for several yeare found satisfactory in Ostwald's laboratory at Leipzig.

These crucibles differ but little in shape from ordinary crucibles. They taper slightly downwards and have a flat bottom with narrow perforations, upon which there fits a removable sieve-plate. They were made at first only of platinum, but they are now to be had of porcelain in several sizes, and are very cheap. Platinum crucibles, in addition to the advantage of platinum apparatus in general, have the valuable property that the apertures in the bottom can be made very small and numerous.

Recently crucibles have been made according to G. C. Caldwell's design, which combine the advantages of both materials. The sides of the crucible are made of porcelain, but the removable bottom is of platinum. In order to preserve the porcelain crucibles, it is advisible not to expose them to the direct flame at once, but to heat them first upon a wire grating covered with asbestos paper, as they otherwise occasionally crack. In order to prepare the crucible for filtering, a cushion of prepared asbestos is placed at the bottom. This is effected by securing the crucible in a glass funnel by means of a very thin caoutchouc pipe, of corresponding width, connected with an aspirator tube. The asbestos (the preparation of which I describe below), is shaken up to a very thin pulp with much water in a small flask; this pulp, after the pump has been set in action, is poured into the crucible in a thin stream. After the water has run off, the bottom is covered with a uniform closely fitting layer of asbestos, which must be so thick that the apertures do not transmit light if the bottom is held up to the window. The perforated plate is then placed in the crucible, and a little water is poured through the filter (preferable from a flask, and not from the jet of a washing bottle, which disturbs the asbestos unnecessarily) until it runs off perfectly clear. Finally, it is gradually heated to incipient redness and weighed.

If the crucible is to be used for filtering, it is again connected with the funnel and the air-pump. The latter must be set in action before the liquid is poured into the funnel. The precipitates are washed as completely as possible by decantation. If the nature of the precipitate allows, very large quantities of water may be used, as it runs through the filter very quickly, and yet perfectly clear. The precipitate may be dried in the crucible, and at any desired temperature. Asbestos is particularly suitable as a filtering material, as it is not at all hygroscopic, and an asbestos filter dried at 100° weighs exactly as much as one heated to redness. Hence, and because when using the Gooch crucible no organic substance comes in contact with the substance, it is especially adapted for determinations in which ignition is either inadmissible or the burning paper may act upon the precipitate. This is the case with determinations of mercury, arsenic, silver, antimony, zinc, &c. Cobalt and nickel may also be very well determined in this manner; for these metals the circumstance is very important that the precipitates, after ignition, may be conveniently washed again. If the ignition has to be effected in an atmosphere of hydrogen, oxygen, carbon dioxide, &c., the lid of the crucible is simply perforated as in a Rose crucible.

In order to prevent the direct action of the gases of combustion, the crucible is placed in a larger one with a massive bottom. Still more convenient is a platinum plate with a high edge, in which the crucible is placed.

The asbestos is prepared by taking soft long asbestos and clipping it in short pieces with scissors. It is then boiled with strong pure hydrochloric acid, freed from all fine particles by washing on a sieve, and finally dried at the common temperature.—*Zeitschrift für Analytische Chemie.*

**Existence of the Diamond in the Meteoric Iron of Cañon Diablo.**—C. Friedel.—After the author's researches there can be no doubt as to the existence of diamond in meteoric iron. This is the first time that this precious stone has been found in what may be considered its primitive gangue. In all the rocks where it has been hitherto met with, even in the pegmatite of India, we may see that it has been introduced as such during the formation of the rock. Here, on the contrary, the very state of the diamond, which appears as a fine powder disseminated in certain parts of the meteoric iron, seems to indicate that it has taken its origin on the spot, and has been formed during the consolidation or the crystallisation of the mass.—*Comptes Rendus*, cxv., No. 24.

# ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.*

By H. N. STOKES.

If a little powdered anhydrous aluminium chloride be added to some ethyl trichlorsilicate, $SiCl_3(OC_2H_5)$, which is cooled by ice, it dissolves, but no reaction is observed; on removing from the ice bubbles of gas soon appear, and the reaction often becomes violent, attended by heating of the liquid. The gas, which burns with green edged flame and formation of hydrochloric acid, is obviously ethyl chloride. If now the liquid be gently heated it gradually becomes thick, then solid, and finally the entire amount of aluminium chloride sublimes unchanged.

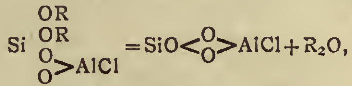
If instead of trichlorsilicate, tetraethylsilicate, $Si(OC_2H_5)_4$, be used, the reaction is in many respects the same, including the formation of ethyl chloride and the thickening of the liquid; but if the test-tube be connected with a condenser, it is seen that much ethylether is also produced. It may also be noticed that a relatively much greater amount of aluminium chloride than in the first case is required to produce the solid residue, while, unless a very considerable quantity has been added, none sublimes out on further heating.

It will be shown below that the action of the aluminium chloride on the trichlorsilicate is a case of so-called *catalytic action* (this being defined as a change brought about by a substance which at the end remains unaltered), while its action on the tetraethyl ether is one which is purely proportional to the relative amounts of the reagents, the aluminium remaining finally in combination with silica. It will also be seen that the monochlorsilicate, $SiCl(OC_2H_5)_3$, is intermediate in its behaviour, a mere trace of aluminium chloride being sufficient to carry the decomposition to an end, when all the aluminium is found in fixed form. From these observations may be deduced the explanation of each case, including the catalytic action of the chloride on the trichlorsilicate. The details of the experiments, which were roughly quantitative, will be found in a separate section.

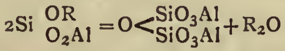
The only hypothesis which explains the facts observed is that in each case the substances react in a truly chemical sense, ethyl chloride and aluminium silicate compounds, Si—O—Al, being formed, but that in case of the chlorsilicates these bodies are exceedingly unstable, and decompose at once with regeneration of aluminium chloride, which is thus able to act again, and thus produce total decomposition when present even in traces.

The cause of this regeneration I take to be due, in part at least, to the tendency of the silicon to monopolise the oxygen, at the expense of the aluminium, forming Si=O, Si—O—Si, &c., whereby the metal is unable to remain combined with oxygen as long as this tendency of the silicon is not fully satisfied. It it happens that the latter is partly combined with chlorine (silicon chlorine), it at once exchanges it for an equivalent of oxygen. This, however, holds only in the aliphatic series of ethers, and in those cases where the chlorine is not the only constituent of the silicon compound. As I shall show elsewhere, silicon, when completely saturated with chlorine, as in silicon tetrachloride, does not show this tendency, neither does it exist in case of the aromatic silicates. From the latter, aluminium chloride, if in excess, takes all the oxygen, and the silicon becomes completely chlorinated.

The formation of *ethyl ether* I can explain only by assuming in silicon a well-known property of carbon, which is manifested in the ortho-ethers of carbonic and other organic acids, namely, that the highest basicity is shown only when all the basic radicals are organic, while the metallic salts are of a lower degree of saturation, and the mixed organic metallic ortho-salts are so unstable as to be scarcely capable of existing under ordinary conditions. Assuming this analogy to exist, we should expect to find transformations like the following occurring:—



$$\mathrm{Si}\begin{matrix}\mathrm{OR}\\ \mathrm{OR}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\!\!>\mathrm{AlCl}=\mathrm{SiO}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{AlCl}+R_2O,$$



$$2\mathrm{Si}\begin{matrix}\mathrm{OR}\\ \mathrm{O_2Al}\end{matrix}=\mathrm{O}\!<\!\begin{matrix}\mathrm{SiO_3Al}\\ \mathrm{SiO_3Al}\end{matrix}+R_2O$$

Strictly speaking, the tendency is not to form, as in the case of carbon, meta-compounds containing Si=O, the analogue of carbonyl, but groupings in which two silicon atoms are united by oxygen, Si—O—Si, or $(SiO)_x$. This tendency is so strong, as has been pointed out by others (*i.e.*, Mendeleeff, *Crundlagen der Chemie, deutsch.*, Aufl. 767), that it is obviously the explanation of the fact that nearly all silicon compounds containing the analogue of carbonyl are not volatile, or volatile only at high temperatures, when by analogy with carbon the reactions producing them should give volatile bodies of low molecular weight. This tendency to condensation and polymerisation by means of oxygen is the rule in the silicon series, and forms one of the most marked differences in the chemical behaviour of these two elements, and the chief obstacle to producing by any simple means definite derivatives of silicic acid. I wish to be distinctly understood, therefore, as using the following formulæ and equations only as typical ones reduced to the simplest possible form, the actual ones being vastly more complex and of almost infinite variety. Where R is used it stands, for sake of simplicity, for ethyl. That the quantitative experimental results do not conform with absolute strictness to the theoretical explanation is not surprising, for aluminium chloride is an extremely reactive body, tending to produce all sorts of secondary changes, while it is not to be expected that the transformations could be carried quantitatively to an end by heating the viscous and finally solid masses which result.

*Ethyl trichlorsilicate*, $SiCl_3(OR)$, is readily and completely decomposed by aluminium chloride, and the reaction is quite independent of the amount used, even a trace being sufficient. The products are ethyl chloride, free from ethyl ether, free aluminium chloride unchanged in amount, and finally a solid residue of the empirical composition $SiO.Cl_2$, but which in reality consists of a mixture of all sorts of complex silicon oxychlorides with free silica, the general result being exprpssed by the equation—

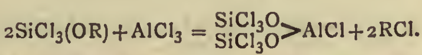
$$SiCl_3(OR)+xAlCl_3=SiO.Cl_2+RCl+xAlCl_3,$$

a typical case of catalytic action.

These oxychlorides are for the most part not volatile, by undergo at high temperature transformation into oxychlorides richer and those poorer in chlorine (Troost and Hautefeullle, *Ann. Chim. Phys.* [5], vii., 469), the result being that they lose weight on ignition. The reactions by which they can be formed in the present case are very numerous, and only a few typical ones are given. The first steps in the process are—

$$SiCl_3(OR)+AlCl_3=SiCl_3.OAlCl_2+RCl,$$

or—

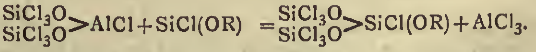


$$2SiCl_3(OR)+AlCl_3=\begin{matrix}SiCl_3O\\ SiCl_3O\end{matrix}\!>\!AlCl+2RCl.$$

These bodies, being for reasons above given very unstable, at once react with fresh portions of trichlorsilicate,—

$$SiCl_3.O.AlCl_2+SiCl_3(OR)=SiCl_3.O.SiCl_2(OR)+AlCl_3,$$

and—



$$\begin{matrix}SiCl_3O\\ SiCl_3O\end{matrix}\!>\!AlCl+SiCl(OR)=\begin{matrix}SiCl_3O\\ SiCl_3O\end{matrix}\!>\!SiCl(OR)+AlCl_3.$$

The regenerated aluminium chloride acts further, thus:—

$$SiCl_3.O.SiCl_2(OR)+AlCl_3=SiCl_3.O.SiCl_2.O.AlCl_2+RCl,$$

---

* From the *American Chemical Journal*, vol. xiv., No. 6.

which latter repeats the process, or may decompose, thus: $SiCl_3.O.SiCl_2.OAlCl_2 = SiCl_3.O.SiO.Cl + AlCl_3$, and so on in every possible way *ad infinitum*, the aluminium chloride being continually regenerated, while the tendency of silicon to such condensations leads to increasing size of the molecules, which tend to the limit $(SiO.Cl_2)x$, but seldom reach it before a high degree of complexity is attained. The increasing viscosity of the liquid interferes with the complete conversion of RO into RCl at a temperature below which other changes set in, which are manifested by more or less evolution of hydrochloric acid and gaseous hydrocarbons, with some carbonisation. There is, however, always an excess of silicon chlorine, which regenerates aluminium chloride, enabling it to act in minute amounts, and to reappear unchanged at the end.

It may be objected that these reactions are purely hypothetical, and that no such compounds as $SiCl_3.O.AlCl_2$ have been shown to exist. In the following cases it will be shown that there is strong evidence of their existence, the aluminium being caught in the act, so to speak, and found ultimately, not as chloride, but in combination with oxygen.

*Ethyl monochlorsilicate*, $SiCl(OR)_3$.—Aluminium chloride, in acting on this compound, produces a similar series of changes, even if used in relatively small amount, with this difference, that as there is not enough silicon chlorine to carry the regeneration through to the end, the aluminium remains finally as $Al_2O_3$, and probably also as AlCl, combined with silica. The process is also complicated in certain cases by the formation of ethyl ether, which was explained above.

If we suppose the aluminium chloride to act by contact or influence merely, the decomposition would be expressed by the equation—

$$SiCl(OR)_3 + xAlCl_3 = SiO_2 + RCl + R_2O + xAlCl_3,$$

and the result would be practically independent of the amount of chloride used, which could be finally recovered unchanged. It is found, however, that while a mere trace is sufficient to bring about total decomposition in nearly the sense of the last equation, by increasing the amount more ethyl chloride and less ethyl ether are formed; when a certain proportion is reached, the ethyl ether vanishes, and also up to this point all aluminium remains fixed in the residue. If more than this amount of chloride be taken, some remains unchanged, and may be recovered by sublimation. We may consider three distinct cases, with differing proportions of the reagents, namely, when

$$Si : Al \begin{cases} > 3 : 2 \ (1) \\ = 3 : 2 \ (2). \\ < 3 : 2 \ (3) \end{cases}$$

The first case includes that where aluminium chloride is present only in traces, when the complete reaction, reduced to the simplest form and neglecting aluminium, would be—

$$(a) \qquad SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

By increasing the proportion of chloride we have, for example,—

$$20SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_{20}(Al_2O_3) + 26RCl + 17R_2O,$$
$$6SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_6 (Al_2O_3) + 12RCl + 3R_2O,$$
&c.

It will be noticed that the relative amount of $R_2O$ decreases, and that of RCl increases as we approach the ratio Si : Al = 3 : 2. Reaching this point, which is case (2), we have—

$$(b) \qquad 3SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_3(Al_2O_3) + 9RCl.$$

The experiment shows that with this ratio no $R_2O$ is formed, and that all aluminium remains in fixed form in the residue.

(To be continued).

# NOTICES OF BOOKS.

*The Coal-tar Colours.* With especial Reference to their Injurious Qualities and the Restriction of their Use. A Sanitary and Medico-Legal Investigation. By Theodore Weyl. With a Preface by Professor Sell. Translated, with permission of the Author, by H. Heffmann, M.D., Ph.D. Philadelphia: Blakiston, Son, and Co. London: Kegan Paul, Trench, Trübner, and Co., Limited.

A careful investigation of the physiological action of the coal-tar colours has now for some time been a desideratum. This want has been, generally speaking, supplied by the author. The information given is exceedingly valuable, though we may venture to express our regret that the terminology employed is not more in harmony with that current in Britain. It is apt to set our teeth on edge to find arsenic spoken of as "arsenicum," and magenta almost invariably as "fuchsin," or sometimes "fuschin." The word "noodles" will puzzle any English reader who is not versed in German. The ordinary English name for that preparation, which the Germans call "nudeln," is vermicelli. The English names for those styles in calico printing which the French name *reservage* and *enlevage* are respectively "resists" and "discharges."

The author shows that the dread of the coal-tar colours, so sweepingly and sensationally expressed in newspaper paragraphs, is exaggerated, and in many cases altogether groundless. A few of these colours, such as picric acid, dinitrocresol, and Martius yellow, safranin, and methylene blue, are distinctly poisonous; whilst aurantia is, to say the least, doubtful. Magenta and the triphenylmethane colours generally are harmless if not contaminated with arsenic or mercury. Samples of these colours made by the old arsenical process are, of course, to be avoided, as are also such by-products as cerise.

Still, we must bear in mind that new coal-tar colours are being constantly invented and introduced into commerce, and that the confectioner and the wine merchant will employ such colours before chemists and physicians have had sufficient opportunity to decide on their composition and their physiological action. Our opinion is therefore in substantial agreement with the Austrian law, that the use of all the artificial colours ought to be prohibited in the preparation of foods and beverages. For such purposes, surely, the natural colours are amply sufficient. Dr. Weyl suggests, indeed, an international poison law for the whole of Europe.

From the abstracts of the legal enactments in force in different countries concerning the use of poisons in the preparation of foods and drinks, the British regulations are made to appear more efficient and more rational than is really the case. The penalty certainly must not exceed £50 for the first offence, but there is no minimum limit. Hence a sympathising magistrate may reduce the penalty to a mere nominal sum! Quite similar is the case with the "hard labour" for a term not exceeding six months. Would it ever be really inflicted?

Among the colours permitted in Austria-Hungary we find mention of "orlean," which is explained as "an infusion of yellow wood (probably fustic?) with one-fourth of alum and of gum." Orlean is generally used on the Continent to signify annatto!

Safflower is given as a permissible yellow colour. The flower certainly contains a yellow colouring matter, but it has little beauty.

The author's endeavours to find a relation between chemical constitution and physiological action are highly to be appreciated, and will, we hope, be successfully followed up.

*Johnston's Catechism of Agricultural Chemistry.* From the Edition Dr. Sir Charles A. Cameron. Revised and enlarged by C. M. Aikman, M.A., B.Sc., F.R.S.E., F.I.C., &c. Ninety-second thousand. Edinburgh and London: William Blackwood and Sons, 1892.

This work, so long and so justly a favourite, is in the present edition brought fairly up to the standard of our present knowledge of agricultural chemistry. It will be perceived that the authors, whilst fully recognising the value of lime in the form of gypsum on certain soils and for certain crops, are far from accepting the exaggerated importance ascribed to it by certain French authorities.

The question of the direct utilisation of atmospheric nitrogen by growing crops is not discussed here, being doubtless considered more suited for advanced students.

The use of ferrous sulphate as a dressing for land is here less favourably judged than it is by Dr. Griffiths. The view laid down in the present treatise agrees better with the general experience of farmers.

We find here no mention of the great advantage derived from the use of basic iron slags as an economical phosphatic manure.

The authors have—very judiciously in our opinion—retained the older and more familiar names for the chemical compounds used or met with in farming, to avoid perplexing the pupils. It is well pointed out that the object of this book is to teach, not chemistry, but scientific agriculture.

*A System of Instruction in Qualitative Chemical Analysis.* By A. H. Elliott, Ph. D. New York: The Author.

The author, it seems, "has found that chemical manipulation cannot be acquired by the reading of directions in a book alone." We were of opinion that this same conclusion had been reached long previously. Dr. Elliott proposes to train analysts in a very wholesale manner.

The instructor is to stand on a raised rostrum where he can be easily seen by every member of a class which may be one hundred in number! He is to perform the operations, and every student is to do the same at the same moment. We doubt if in case of nicer determinations this method is to be recommended.

As regards the subject matter of the book, we find them neither better nor worse than the instructions to be met with in other analytical manuals.

*The Chemists' Legal Hand-book.* By A Barrister, 1892. London: Offices of the *British and Colonial Druggist.*

This hand-book is designed solely for the information of the dealers in, and compounders of, medicines and poisons, known on the Continent as "apotheker" or "pharmaciens," but in England as "chemists." To the profession known abroad as "chemiker" or "chimistes," and in England devoid of any generally recognised name, it has little to say.

The author contents himself with explaining the law as it is without attempting to point out its many defects or to suggest their attending removal. Due mention is made of that most unhappy modification in the regulations for the preparation of methylated spirit, by which this article is rendered useless for the scientific investigator, without a series of red tape regulations.

A great hardship is also inflicted upon such persons—or would be if the law were carried out, as it may be any day—by the duty upon stills. The law is not limited to apparatus adapted for producing or rectifying excisable liquors, but seems to include every retort of whatever size, shape, or material. Nay, it almost appears to be by the mere grace of the Commissioners of Excise that scientific investigators "may keep and use stills for chemical experiments or for the manufacture of articles other than spirits or spirit-mixtures."

It even appears that persons who have applied for permission to buy methylated spirit free from mixed naphtha have been favoured with very annoying visits from the Excise.

It seems a farce to aim at the development of scientific chemistry and the improvement of our chemical manufactures so long as such barbarous regulations are kept up.

We ought to demand that the laws regarding stills shall be held no longer to apply to retorts, &c., made of glass, porcelain, stoneware, silver, or platinum, and that for such no license shall be required and no duty shall be chargeable. Further, the addition of a trace of Dippel's animal oil to methylated spirit should be introduced instead of mineral oils.

*Elementary Chemical Analysis.* By William Ackroyd, F.I.C. Halifax: Whitley and Booth.

This little pamphlet contains nothing which can be pronounced erroneous or misleading. But, like nine-tenths of the elementary chemical treatises still showering from the press, we cannot see that it was required.

## CORRESPONDENCE.

### ANALYSIS *VERSUS* ASSAYING.

*To the Editor of the Chemical News.*

Sir,—The word analysis is used in many branches of knowledge with a meaning which is brought home to the student of chemistry when his teacher dwells on the difference beween analysis and synthesis. It is a pity for a word of this kind to be degraded. In its passage from the lecture-room to the laboratory, however, it loses all precise meaning. The student is taught that analysis is an art of which only a few of the operations are analytical; he is taught to speak without blushing of the analysis of an element. He will learn to analyse sugar with a polariscope and copper with potassium cyanide. The analysis of a sample of butter can be made by determing its refractive index. Is it any wonder, then, that he comes to believe that whatever an analyst may choose to do is analysis, and that there is no use at all for the word assaying?

And yet this word assaying is a good English one, and has a vigorous existence. Long may it be so. And if the time must come when it will be used no longer, then may "trying" and "testing," which are its nearest representatives, be its successors.—I am, &c.,

J. J. Beringer.

### THE POSITION OF CHEMISTS.

*To the Editor of the Chemical News.*

Sir,—If you will allow me to join in the discussion on the position of chemists I think I can give an explanation of why a chemist in many cases receives a low salary. To put it plainly, in the majority of instances he is not worth more than he gets. We chemists must not blind ourselves to the fact that our chemistry in itself is absolutely useless in most branches of commerce; it is the application of chemistry to commerce that is of infinite importance. We may compare chemistry to a foreign language in which invaluable facts are recorded; a man who is fully conversant with this language is of no value unless he can interpret it into "a tongue understanded of the people." The chemist to whom a low salary is paid is one who is not yet an efficient interpreter; when he has perfected himself in this, his salary will rise; aye, and rise rapidly.

Is organisation (attractive delusive word) likely to force men, who know what they want, to pay men who can't give this to them large salaries? Would a Constantinople firm pay a Turk who could not express himself in English a large salary? No.

The remedy for low salaries is in the hands of individuals. Let the student fresh from college realise how useless he and his degrees are; let him take a low salary, keep his eyes and ears open and work; let him learn everything he can, whether it be engineering, stoking, German, or book-keeping; let him dirty his hands well, and in a few years, if the big salary does not come, he may rest assured that he is a duffer.

I speak from experience. Years ago, when I left college (highly recommended!), I was told by a large employer of chemists that I was only worth five shillings a week to him; and that was the salary he offered me. I did not believe him, and was mightily offended; but after seven months of looking for a berth, I accepted a low salary, and did some years' drudgery and knocking about in the world; to-day I see my salary growing from a respectable one to something better.—I am, &c.,

Caveat Emptor.

## THE POSITION OF CHEMISTS.

*To the Editor of the Chemical News.*

Sir,—I was very pleased to read the letters of "J. B. C." and "Dare Lucem" in reply to mine upon this subject; at the same time I am rather disappointed at the apparent apathetic disposition of chemical brethren generally, whose higher status is aimed at. If anything definite is to be accomplished it must result from general unison of action, for it cannot be expected that one or two willing hands shall build a golden bridge for others.

I clearly see the many difficulties to be contended with, but I do not think there are any insurmountable. As "Dare Lucem" aptly states, the time is gone for rule of thumb methods of manufacture, and practical science is absolutely necessary in order that successful combat may be made with the keen competition now existing. Rule of thumb must be ignored, and experience and practicality be recognised.

It is in our own hands to so formulate a scheme that employers will be pleased to know that they are able to rely upon the services of a chemist recommended to them with a certain amount of guarantee for his abilities and integrity, while chemists themselves will have protection and the dignity of the profession be maintained.

In "J. B. C.'s" letter he expresses a doubt as to the success of such a movement as is now suggested, because of those usurpers who are now so damaging to chemists of experience and ability. I should say that their admission into any such society should be most strenuously opposed, because the fundamental principle of such union of chemists must be that none but those who give positive proof of chemical training and specific practical knowledge shall become members.

If such things come to pass—and I fail to see why not—the usurpers, be what they may, will quickly become no factor in our problem.

I sincerely hope now that some chemists will communicate with me by letter (care of the office of this paper), so that we may at once take up the forming of some satisfactory scheme; and now the enhancement of the brilliant profession of a chemist is being promoted, let there be no apathy shown, but let one and all work with a determination to secure for ourselves what no Chemical Society has yet been able to do.

In conclusion, let me draw attention to the fact that a salary of £80 per annum is £1 10s. 9d. per week, and is practically the same sum as is now being paid to labourers for pulling down bricks and mortar at Millbank Prison. Here is food for reflection.—I am, &c.,

T. H. Davis.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

**Note.—All degrees of temperature are Centigrade unless otherwise expressed.**

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxv., No. 24, December 12, 1892.

**Description of a New Electric Furnace.**—Henri Moissan.—(See Chemical News, vol. lxvi., p. 319).

**Action of a High Temperature upon Metallic Oxides.**—Henri Moissan.—This paper will be inserted in full.

**Density of Carbon Monoxide and the Atomic Weight of Carbon.**—A. Leduc.—The density in question is 0·96702; and the atomic weight of carbon = 11·913.

**Critical Reduction of the Fundamental Determinations of Stas on Potassium Chlorate.**—G. Hinrichs. — This paper requires the accompanying diagram. The author's final result is that all the atomic weights of Stas are inaccurate.

**On a Carbon Chloroiodide.**—M. Besson.—The chief chemical characteristic of the chloroiodide, $C\,Cl_3I$, is the ease with which it parts with iodine to form sesquichloride. In the action of aluminium iodide upon carbon chloride, $C\,Cl_4$, there are formed other iodine substitution products, which the author has not isolated in a state of purity. They would be $C\,Cl_2I_2$ (a liquid), and $C\,ClI_3$ (a solid).

**Action of Hydrofluoric Anhydride upon the Alcohols.**—Maurice Meslans.—Below 130° hydrofluoric anhydride has no perceptible action upon absolute alcohol. Etherification is most conveniently effected at 220°.

**Action of Sulphuric Acid upon Citrene.**—G. Bouchardat and J. Lafont.—The portion of citrene not attacked by the acid is a saturated carbon, $C_{20}H_{22}$. It boils at 165—168°. The sulpho-conjugated acid, if saturated with baryta, yields barium sulphocyanate, $C_{20}H_{13}BaS_2O_6+3HO$, and a much more soluble salt, $C_{18}H_{14}BaS_2O_6+2H_2O_2$. A third salt is present in a quantity much too small for analysis.

**Assay of Quinine Sulphate, and Determination of Quinine in Presence of the other Alkaloids of Chinchona.**—L. Barthe.—This paper will be inserted in full.

Vol. cxv., No. 25, December 19, 1892.

This issue gives an account of the Annual Public Session, held on December 19th. It comprises the discourse of the President, M. d'Abbadie, in praise of deceased members and foreign associates of the Academy. Then follow the reports of the various commissions nominated to adjudicate on the memoirs presented in competition for the numerous prizes at the disposal of the Academy. Among the prizes offered for future research, we mention that founded by Dr. Jecker, *i.e.*, a sum of 10,000 francs, to be awarded each year for the most important discovery calculated to accelerate the progress of organic chemistry.

*Journal fur Praktische Chemie.*
New Series, Vol. xlvi., Part 1.

**On Hexamethylenamine.** — L. Hartung. — The author has examined the action of benzoyl chloride and acetyl-chloride upon hexamethylenamine, the action of monochloracetic ethyl ester, that of monochloracetic ether upon hexamethylenamine in an alcoholic solution, the behaviour of inorganic acids upon hexamethylenamine, the action of sulphurous acid upon hexamethylamine dissolved in benzene, the action of the same compound in isobutylic alcohol, in isopropylic alcohol, in methylic alcohol; the action of nitrous acid upon hexa-

THE CHEMICAL NEWS.

VOL. LXVII., No. 1729.

# DETERMINATION OF IMPURITIES IN METHYLENES.

By ER. BARILLOT.

IT is very important to ascertain in the industrial methylenes intended either for the methylation of aniline, or for the denaturation of industrial alcohols, the proportion of impurities, other than acetone, which these methylenes contain. The following method yields good results:—

*Principle.*—1. On agitating 20 c.c. of chloroform with a mixture formed of 10 c.c. of methylic alcohol, 15 c.c. sodium bisulphite of sp. gr. 1·325, and 5 c.c. of water, the coefficient of separation between the two non-miscible liquids is such that the chloroformic stratum preserves its entire volume if the methylic alcohol contains no other impurities than acetone. 2. If the methylic alcohol contains impurities (benzols, methylol, diallyl, &c.), the chloroformic stratum increases in proportion to their quantity.

*Application.*—1. Into a tube, *a*, of about the capacity of 40 c.c., we pour 10 c.c. of the methylene in question, then 15 c.c. of the solution of sodium bisulphite, stopper the tube, and shake it strongly. We add then 5 c.c. of water, shake up afresh, and allow the mixture to resume the ordinary temperature. 2. A glass tube of the capacity of 10 c.c., terminating below in a cock, communicates at its top by a narrower tube graduated in c.c.'s and tenths of a c.c., with a glass globe, *b*, holding about 200 c.c., the upper tubulure of which can be closed with a ground glass stopper.

Into this apparatus, *b*, we pour chloroform so as to fill the lower tube, the capacity of which is exactly 20 c.c. The meniscus of this liquid is then exactly level with the zero of the graduation into c.c. and tenths of a c.c. at the temperature 15°.

The mixture in *a* is poured into the apparatus *b*; we shake strongly, so as to obtain an emulsion of milky appearance and allow it to settle.

When the two liquid strata of the apparatus *b* are quite clear, we read off at 15° the increase of the volume of chloroform. This increase, multiplied by ten, corresponds to the percentage of impurities, other than acetone, contained in the methylene.

The alcoholometric of the methylene examined may be comprised between 80° and 99°. The proportion of acetone, from 1 to 30 per cent, does not affect the accuracy of the determination.

Having isolated the impurities which accompany methylene, we have made up a great number of synthetic samples with pure methylic alcohol, pure acetone, and the isolated impurity in order to check the accuracy of the procedure.

The results obtained with the various types of synthetic commercial methylenes are:—

| | | Impurity per cent. |
|---|---|---|
| A | Methylic alcohol, chemically pure .. .. | 0 |
| | Pure industrial methylic alcohols used for the methylation of aniline .. .. | 1 to 2 |
| B | Methylenes, pure Government types, with 20 per cent acetone .. .. .. | 1 to 2 |
| | Methylenes, pure Government types, with 5 p.c. impurity and 2 p.c. acetone | 5 |
| C | Strong smelling methylenes, with 10 per cent impurity .. .. .. .. .. .. | 10 |
| | Very strong smelling methylenes .. .. | 15 to 20 |

With the type B the denaturation is illusory, whilst with the types C the denaturation of the industrial alcohols is real.

The examination of a great number of samples of the methylenes of commerce has shown that often the denaturising impurities do not exceed 2 to 5 per cent, and that the methylenes which really denaturise alcohol contain from 10 to 20 per cent of these impurities.

The examination of the chloroformic stratum enables us to determine the nature of the impurity.—*Comptes Rendus.*

# SEPARATION OF MICRO-ORGANISMS BY CENTRIFUGAL ACTION.

By M. R. LEZÉ.

THE micro-organisms comprise chiefly in their constitution substances heavier than water; these are the albumenoid, cellulosic, and mineral substances, which are isolated by incineration. If the living organisms float in liquids such as wine, cider, or milk, the specific gravity of which borders closely upon unity, it is because they probably contain small quantities of gas, and the force which impels them to rise or sink in a liquid heavier or lighter than their protoplasmic substance is certainly very feeble, regard being had to the very small dimensions of these bodies in question.

But we may intensify this tendency to separation by submitting vessels containing fermentable liquids and organisms to rapid rotatory movement. We have the centrifugal force at command, and can render it several hundred times greater than the intensity of gravitation.

In the laboratory appliances which we employ, the radius and the speed are: in the "lactocrit" turned by hand, 9 c.m. and 3600 rotations; in the steam turbine (Burmeister's design), 20 c.m. and 4000 rotations.

In the former apparatus the recipients submitted to centrifugal force are small tubes, drawn out for a certain length in a conical form, and sealed before the lamp at the point. The second apparatus is continuous, and enables us to whiz indefinitely increasing quantities of the liquid in question.

Rotation clarifies fermenting liquids and determines the formation of a glutinous or gelatinous deposit, either at the points of the small tubes or upon the sides of the turbine. On examining these muddy deposits under the microscope, we perceive that they consist chiefly of a heap of living organisms.

By this method we have separated the organisms from a considerable number of liquids in course of fermentation by submitting to the centrifugal zone musts in course of fermentation, decoction of hay, milk or its serum, after the separation of the cream or of the curd, saccharine liquids loaded with moulds, wines in acetic fermentation, &c. The organisms appear to separate the more easily the larger are their dimensions. We can very distinctly isolate the mycelium and the spores of mould and the saccharomyces, whilst bacteria are only imperfectly separated.

In one of the experiments we passed fermenting cider. The liquid was turbid, but it became perfectly limpid. Samples collected in open or sterilised bottles, and kept in the stove at 30° all became turbid the next day, and swarmed with bacteria. Yeasts were no longer found, and the alcoholic fermentation had disappeared.

In order to facilitate the separation we may either heat the liquid or add liquids lighter than water, such as ammonia or alcohol. This separation of bacteria may find an application in bacteriological research. In industrial practice we may, perhaps, by means of centrifugal force free polluted or insalubrious waters from the greater part of the organisms present, being careful to admit into the turbine no air but such as has been filtered through a thick layer of cotton.—*Comptes Rendus.*

## THE DECOMPOSITION OF TIN SLAGS BY THE FLUORIDE METHOD.

By H. N. WARREN, Research Analyst.

The decomposition of siliceous slags containing the oxides of tin and antimony was, up to a comparatively recent date, brought about entirely by fusing the same with a mixture of carbonate of sodium and potassium; the tediousness and prolongation of the operation, however, induced the author to use borax as a fluxing agent in admixture with the carbonates. And so rapid and complete was the decomposition of these refractory substances that the operation soon became employed in most of the leading laboratories throughout the kingdom. A more accurate method, however, is still in readiness, oxides of tin and antimony having lately been proved to be by no means fixed when subjected to high temperatures in contact with alkalies; and in numerous instances the fumes collected by volatilisation from the crucibles containing these substances were found on examination to retain notable percentages of both tin and antimony; the nickel vessels employed are also liable to introduce further errors.

In employing the fluoride method, a convenient portion of the slag in a fine state of division is introduced into a platinum dish of suitable dimensions, and acted upon by an equal portion of hydrofluoric and hydrochloric acids, a gentle heat from a sand-bath being applied for a few moments. The slag almost immediately passes into solution, the solution thus obtained is diluted to a known volume, one-half being precipitated by the addition of $SH_2$. The precipitated sulphides of tin and antimony thus obtained, after purifying if necessary by re-solution, are ignited and weighed as oxides.

The second half having been rendered alkaline by means of ammonia, a large excess of oxalic acid is added in order to re-dissolve the precipitate, the introduction of $SH_2$ in excess being maintained as before. Antimony sulphide alone falls, which is ignited and weighed as oxide. From the previous weight of the mixed oxides the percentage of antimony is at once obtainable by subtracting the latter.

By this method a complete separation and estimation of both metals can be performed in less than an hour, over three hundred samples of a like nature having been worked by this method during the past year to an accuracy of decimal 2 per cent.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

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## ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.*

By H. N. STOKES.

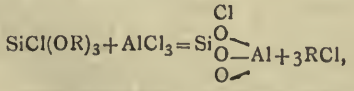
(Continued from p. 10).

Any further increase in the proportion of chloride belongs under case (3), where $\mathrm{Si : Al} < 3 : 2$. For example, if the ratio be that of equality, or 3 : 3, we might have—

(*c*) $\quad 3\mathrm{SiCl(OR)_3} + 3\mathrm{AlCl_3} = \mathrm{(SiO_2)_3(Al_2O_3)} + \mathrm{AlCl_3}.$

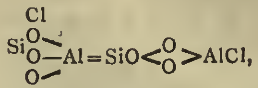
In fact, when this proportion is taken, unchanged aluminium chloride sublimes out of the residue. Owing, however, to the tendency of the silicon to monopolise the oxygen or to take the metasilicate form, this proportion admits of another reaction :—

(*d*)



$$\mathrm{SiCl(OR)_3+AlCl_3=Si}\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\diagdown\\ \mathrm{O}-\\ \mathrm{O}\diagup\end{matrix}\mathrm{Al+3RCl},$$

and



$$\mathrm{Si}\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\diagdown\\ \mathrm{O}-\\ \mathrm{O}\diagup\end{matrix}\mathrm{Al=SiO}<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}>\mathrm{AlCl},$$

the residue being a chloraluminium metasilicate, or at least some similar form in which the preference of silicon for oxygen before chlorine is satisfied. The chlorine and aluminium in this form are practically fixed, as such a body as this would probably give off aluminium chloride, if at all, only at a high temperature, the effect being that the volatile chloride falls below the theoretical amount required by equation (*c*).

Finally, if Si : Al = 1 : 2—

(*e*) $\quad \mathrm{SiCl(OR)_3} + 2\mathrm{AlCl_3} = \mathrm{SiO_3Al_2Cl_4} + 3\mathrm{RCl}.$

If we write the formula of the product—

$$\mathrm{SiO}<\begin{matrix}\mathrm{OAlCl_2}\\ \mathrm{OAlCl_2}\end{matrix},$$

it appears that in this form also the aluminium might be fixed, but that if more chloride be present, leading to the formation of $\mathrm{SiCl(OAlCl_2)_3}$, such a body would, by virtue of the silicon chlorine present, decompose at once into $\mathrm{AlCl_3}$ and $\mathrm{SiO(OAlCl_2)_2}$. Two atoms aluminium are therefore the most that can possibly be held by one atom silicon reacting as monochlorsilicate; any further amount must remain finally as unchanged chloride. The stability of such bodies as $\mathrm{SiO(OAlCl_2)_2}$ is, however, made improbable by the experiments, which show that even with the ratio 1 : 1 only a part of the aluminium remains fixed.

These equations do not explain the semi-catalytic action of aluminium chloride in decomposing indefinitely large amounts of monochlorsilicate. The reason is obvious when we consider that, as the experiments show, the greatest amount of aluminium which can be held fixed by 1 mol. wt. monochlorsilicate, lies between $\frac{2}{3}$ and 1 at. wt. (equations *b* and *d*). Any greater amount of monochlorsilicate will, by virtue of its silicon chlorine, regenerate aluminium chloride, and be destroyed thereby, until the above proportion is reached. At this point further reaction results only in the sense of *b* and *d*, the regeneration of the chloride ceases, and all aluminium remains fixed.

It will be observed that in these reactions the chlorine going to form ethyl chloride comes proximately from the aluminium chloride, but ultimately in part from the chlorsilicate, and that the equations—

$$\mathrm{SiCl_3(OR)} = \mathrm{SiOCl_2} + \mathrm{RCl},$$
$$\mathrm{SiCl(OR)_3} = \mathrm{SiO_2} + \mathrm{RCl} + \mathrm{R_2O}$$

are not strictly true, the aluminium acting as the agent by which Cl is transferred from Si to R. The hypothesis might perhaps be further tested by substituting aluminium bromide for the chloride. If the decomposition is due to *influence* only, $\mathrm{SiCl_3(OR)}$ should give $\mathrm{SiOCl_2}$, and RCl, and $\mathrm{AlBr_3}$ only, but on the above hypothesis $\mathrm{SiO.Cl_2}$ with either RBr and $\mathrm{AlCl_3}$ only, or a mixture of RCl, RBr, $\mathrm{AlCl_3}$, and aluminium chlorobromides, according to the proportions and the nature of the intermediate products. As this would involve previously studying the question whether a *direct* interchange of chlorine and bromine might occur, the experiment was postponed.

*Ethyl dichlorsilicate*, $\mathrm{SiCl_2(OR)_2}$, from similar considerations, should decompose thus—

$$\mathrm{SiCl_2(OR)_2} = \mathrm{SiO_2} + 2\mathrm{RCl},$$

and it is not possible to devise any probable reaction by which aluminium should remain permanently combined. Therefore the apparent catalytic action should be as obvious here as in the case of the trichlorsilicate. The experiments were, however, defective, probably owing to impure material, and no satisfactory conclusion could be drawn from them.

*Ethyl orthosilicate*, $\mathrm{Si(OR)_4}$. — This body shows a radically different behaviour from that of the chlorsilicates,

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* From the *American Chemical Journal*, vol. xiv., No. 6.

the decomposition being strictly proportional to the relative amount of aluminium chloride used, and in this lies the explanation of the whole series of observations.

We may consider the following cases:—

$$\mathrm{Si:Al}\begin{cases} <3:4 & (1)\\ =3:4 & (2)\\ >3:4 & (3)\end{cases}$$

the ratio 3 : 4 being that in which the aluminium chloride contains just enough chlorine to convert all ethyl into ethyl chloride.

(*a*) $3Si(OR)_4+4AlCl_3=Si_3O_{12}Al_4+12RCl.$

From considerations mentioned while speaking of the monochlorsilicate, it is obvious that this proportion may result in a certain amount of chlorine remaining combined with the aluminium up to the limit—

(*b*) $3Si(OR)_4+4AlCl_3=Si_3O_{10}Al_4Cl_4+8RCl+2R_2O.$

For practical reasons given below, the substances could not be made to react in this proportion, the result being a formation of ethyl ether, ethyl chloride, and sublimation of some unchanged aluminium chloride. For the same reason a reaction in the sense of case (1) was practically not to be brought about.

If the reaction were in any sense catalytic, it would follow that by reducing the aluminium chloride below the proportion Si : Al = 3 : 4, the decomposition would still be complete, but the amount of ethyl ether would increase relatively, while that of ethyl chloride would decrease, the limit being, with a trace of aluminium chloride—

$$Si(OR)_4=SiO_2+2R_2O.$$

The actual result was that while with Si : Al = 3 : 1 the decomposition was complete, and approximately in the sense—

(*c*) $6Si(OR)_4+2AlCl_3=(SiO_2)_6(Al_2O_3)+6RCl+9R_2O,$

the slightest diminution of the amount of chloride below this ratio was followed by some of the silicate remaining totally unchanged. With Si : Al = 3 : 0·9, for instance, it was possible to recover some of it, and with Si : Al = 150 : 1 the merest trace of decomposition was discernible. This proportion in the case of the monochlorsilicate resulted easily in total decomposition. The only possible explanation of this difference is that in the case of the chlorsilicates the apparent contact action is due to constant regeneration of aluminium chloride by silicon chlorine. The tetraethyl ether contains no silicon chlorine, aluminium chloride is not regenerated, and therefore acts only in proportion to the amount originally taken.

An experiment was made which shows the peculiar stability of silicon tetrachloride as compared with the chlorsilicates. It was supposed that since

$$SiCl_3(OR)+\text{trace }AlCl_3=SiO.Cl_2+RCl+\text{trace }AlCl_3,$$

by adding to tetraethyl silicate some silicon tetrachloride in the proportion required by the equation—

$$Si(OR)_4+3SiCl_4=4SiCl_3(OR),$$

the chlorine of the tetrachloride would regenerate aluminium chloride, with the final result that solid silicon oxychloride and ethyl chloride would be formed. With even Si : Al = 5 : 1, and in sealed tubes at 100°, no solid was formed. Only after heating at 170°, at which temperature the tetrachloride acts on the ether, did total decomposition occur.

Anhydrous ferric chloride acts on both the tetraethyl silicate and the trichlorsilicate, but with much greater difficulty than aluminium chloride. Only at near the boiling-point (105°) of the trichlorsilicate was any marked reaction, with formation of ethylchloride, visible. The tetraethyl silicate reacted easily on heating, giving off ethyl ether and ethyl chloride and leaving a solid residue. The reactions were not further studied.

Anhydrous zinc chloride is without action on the tetraethyl silicate at its boiling-point (165°).

(To be continued).

## REPORT ON THE TECHNICAL DETERMINATION OF ZINC.*

(Concluded from p. 7).

*Method of Mr. Mann Page, Chemist Omaha and Grant Smelting Company, Denver, Colorado.*—The ore is decomposed by boiling in a casserole with a mixture of concentrated hydrochloric, nitric, and sulphuric acids, added separately in the order given, the amounts of acid varying according to the demands of the character of the ore under treatment to ensure complete decomposition. The boiling is continued until the fumes of sulphuric acid appear distinctly.

The casserole is then removed from the hot plate, contents allowed to cool, and the sulphuric acid solution diluted with water to three or four times its bulk, and chlorate of potassium added whether manganese be present or not.

If manganese is present, the chlorate must be added in quantity sufficient to ensure complete precipitation, an additional quantity of this reagent being added during the boiling if it appears necessary. This can be easily determined by the appearance of the solution. The precipitated manganese dioxide and the insoluble residue are now filtered off and well washed with boiling water.

To the filtrate ammonia water is added *in slight excess*, the precipitate well stirred, and immediately filtered off, the filtrate passing into a graduated flask of 250 c.c. capacity.

After the iron and alumina precipitate has been transferred to the filter—which should be a sufficiently capacious one—it is allowed to drain thoroughly, and then washed three or four times with water which has been rendered distinctly ammoniacal, and which should not be more than *tolerably* warm. In washing the precipitate care should be taken to thoroughly disintegrate it by the stream of wash water.

After a thorough washing, the filtrate is acidified by hydrochloric acid, the flask filled to the mark, its contents well mixed, and a number of aliquot portions of the solution taken from the zinc determination, which is accomplished by a standardised solution of ferrocyanide of potassium, acetate of uranium being used as indicator.

If copper be present, it must be removed previous to titration by means of granulated lead. The titration is always made in hot solutions.

Results were as follows:—

| | | |
|---|---|---|
| No. 5.. .. .. | 14·62 | per cent zinc. |
| „ 9.. .. .. | 22·00 | „ „ |
| „ 11.. .. .. | 10·50 | „ „ |
| „ 13.. .. .. | 6·30 | „ „ |
| „ 20.. .. .. | 15·37 | „ „ |

Notes on the above method:—

Attention has been called to the advisability of washing the iron precipitate with water which is not more than tolerably warm, it having been the writer's experience that a partial precipitation of the hydrated oxide of zinc takes place more easily from solutions which, while yet distinctly ammoniacal, approach more nearly the boiling temperature. The precipitation of the hydrated zinc oxide is furthermore influenced by the precipitation of the hydrated sesquioxide of iron, especially so when the solutions are very hot.

To prevent this occurrence the precautions previously indicated must be observed, in addition to which, as a further safe-guard, wash water, which has been rendered ammoniacal, or has been impregnated with chloride of ammonium is used.

*Method of Mr. F. Mentzel, Superintendent San Juan Smelting and Mining Company, Durango, Colorado.*—The method about to be described is based on the principle that in an almost neutral solution of sulphates or chlorides, the separation of zinc from iron, manganese,

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* A report read at a meeting of the Colorado Scientific Society. From the *Journal of Analytical and Applied Chemistry*, vi., No. 9.

cobalt, and nickel can practically be effected by means of hydrogen sulphide, while if the solution contains about one-tenth of its volume of sulphuric acid the separation of zinc from copper is equally complete, provided the solution is heated almost to the boiling point before the precipitated sulphides are filtered off.

The *modus operandi* is as follows:—

One grm. of ore is decomposed in an eight ounce flask with 5 c.c. conc. hydrochloric and 5 c.c. conc. nitric acid; after the red fumes have ceased to be evolved, 5 c.c. conc. sulphuric acid are added, and the whole evaporated until the fumes of sulphuric acid appear. It is absolutely essential at this point that all traces of nitric acid should have been expelled, as otherwise correct results will be vitiated.

On the appearance of the sulphuric acid fumes the flask is removed from the hot plate, allowed to cool, about 50 c.c. water added, and a brisk current of hydrogen sulphide passed through the solution. In a few minutes the precipitation of the copper, &c., will have taken place. The precipitation is complete when precipitated sulphides are seen to settle rapidly at the bottom of the flask.

Now heat the solution as rapidly as possible almost to the boiling point, by which most of the absorbed sulphuretted acid will be expelled; any zinc which may have been precipitated will by this means be re-dissolved. Filter into a sixteen ounce flask, wash the precipitate with cold water three or four times, allowing the filter to run dry each time before renewing the wash water.

After washing, neutralise the filtrate with ammonia water, care being taken not to let the ammonia run down the sides of the flask, but to drop it directly into the liquid, the solution being constantly agitated while being neutralised. It is advisable to add a slight excess of ammonia, the ferrous hydrate precipitate being again re-dissolved by a few drops of dilute sulphuric acid (1 : 4). A slight permanent turbidity is of no consequence.

Now add an excess of four to six drops of dilute sulphuric acid, fill up the flask with water, and again introduce a brisk current of hydrogen sulphide into the solution. Within five to ten minutes a heavy sandy or powdery precipitate of whitish or yellowish zinc sulphide will appear, the rapid settling of which, and the clear supernatant liquid, being an indication of complete precipitation. The precipitate filters rapidly, and is indifferent to the influence of air, either during filtering or washing. It is filtered off and thoroughly washed, about five washings being usually sufficient unless the solution contained much iron.

The zinc sulphide which has adhered to the flask and the glass tube is now dissolved in 3 to 5 c.c. of hydrochloric acid, the solution diluted with an equal amount of water, and then poured on the filter containing the precipitate, which should immediately thereafter be covered with a watch glass. The greater part of the precipitate dissolves easily, the solution of any undissolved portion being effected with a few drops of conc. hydrochloric acid.

The bulk of free acid in the solution is now neutralised with ammonia water, and the zinc determined by titrating with standardised solution of ferrocyanide of potassium, using acetate of uranium as an indicator.

The following are the results obtained:—

Per cent Zinc.

| | No. 9. | No. 11. | No. 13. | No. 20. |
|---|---|---|---|---|
| | 23·63 | 11·17 | 6·94 | 16·15 |
| | 23·56 | 11·13 | 7·05 | 16·05 |
| | 23·56 | 10·99 | 6·76 | 16·10 |
| | 23·73 | 10·99 | 6·81 | 16·02 |
| Average.. | 23·62 | 11·07 | 6·89 | 16·08 |

*Method of Dr. H. C. Hahn, Chemist Colorado Smelting Company, Pueblo, Colorado.*—The following method is one in which the determination of manganese as well as zinc is effected in the same solution.

Five-tenths of a grm. of ore is treated in a porcelain casserole with 2 c.c. conc. nitric, 3 c.c. dilute sulphuric (1 : 2), and 6 c.c. conc. hydrochloric acids, evaporated to dryness, or until the fumes of sulphuric acid appear. The casserole is then removed from the hot plate and allowed to cool, when 20 c.c. water are added, and the solution heated to boiling for about one minute.

The contents of the casserole are now transferred to an eight ounce beaker, and the solution nearly neutralised with a saturated solution of carbonate of sodium. In case too much of the latter should have been used, acidify with a few drops of dilute sulphuric acid.

Now add to the solution an excess of basic carbonate or lead suspended in water, until after vigorous stirring the precipitated hydroxide of iron settles quickly to the bottom of the beaker, leaving the liquid clear.

The solution should measure now about 80 c.c. It is heated to boiling without previous filtration, and the manganese determined with a standardised solution of permanganate of potassium (4·86 grms. of potassium permanganate to a litre, whence 1 c.c. equals 0·50 per cent Mn).

After each addition of the permanganate the solution should be briskly stirred, as it facilitates the settling of the precipitate. Should the solution appear yellow or turbid, the stirring must be continued until it is clear. When the rose tint appears, indicating the complete precipitation of the manganese, a few grms. of chloride of ammonium and 5 c.c. ammonia water are added, and the solution is filtered without previous heating, the precipitate being washed with water containing about one-fifteenth of its bulk of strong ammonia water.

The precipitate is well washed, and to the filtrate, which should measure about 140 c.c., 12½ c.c. of hydrochloric acid are added. If copper is present, it is removed by means of granulated lead, after which the zinc is determined by titrating with a standardised solution of ferrocyanide of potassium, an uranium salt being used as indicator.

The manganese determination is quite exact, but the zinc determination not so good.

The results on samples of ore submitted are:—

Per cent Zinc.

| | No. 5. | No. 9. | No. 11. | No. 13. | No. 20. |
|---|---|---|---|---|---|
| | 14·38 | 22·95 | 8·58 | 5·24 | 13·40 |
| | 14·22 | 23·11 | 9·20 | 5·64 | 12·84 |
| Average.. | 14·30 | 23·03 | 8·89 | 5·44 | 13·22 |

Per cent Manganese.

| | No. 5. | No. 9. | No. 11. | No. 13. | No. 20. |
|---|---|---|---|---|---|
| | 3·22 | 2·89 | 2·68 | 9·25 | 0·65 |
| | 3·32 | 2·81 | 2·72 | 9·53 | 0·87 |
| Average .. | 3·27 | 2·85 | 2·70 | 9·39 | 0·76 |

Note.—The basic carbonate of lead used in the preceding method is prepared by adding to a hot solution of carbonate of sodium a hot solution of acetate of lead as long as a precipitate is formed, and washing the precipitate repeatedly by decantation until all sodium salts are removed.

*Comparison of Results.*

| Analyst. | No. 5. | No. 9. | No. 11. | No. 13. | No. 20. |
|---|---|---|---|---|---|
| Eakins .. .. .. | 14·64 | 24·11 | 10·71 | 6·31 | 16·09 |
| Von Schulz and Low | 15·31 | 24·34 | 10·76 | 6·42 | 16·14 |
| Jones .. .. .. | 15·39 | 24·53 | 10·83 | 6·58 | 16·46 |
| Hawkins .. .. .. | 15·66 | 24·23 | 11·88 | 8·73 | 15·86 |
| Knight .. .. .. | 15·08 | 23·80 | 10·69 | 6·85 | 15·90 |
| Page.. .. .. .. | 14·62 | 22·00 | 10·50 | 6·30 | 15·37 |
| Mentzel .. .. .. | — | 23·62 | 11·07 | 6·89 | 16·08 |
| Hahn .. .. .. | 14·30 | 23·03 | 8·89 | 5·44 | 13·22 |

A consideration of the above results leads to the conclusion that there are a number of the methods detailed that are satisfactorily adapted for the technical determination of zinc. All of the technical chemists employ the ferrocyanide solution for the final titration.

A method, however, like the one used by Mr Mentzel will hardly commend itself on account of the repeated use of hydrogen sulphide. The unique method of Dr. Hahn for the combined determination of manganese and zinc from one solution is open to the serious objection that the zinc results are uniformly low. With this difficulty obviated, the method would be a highly commendable one.

The governing factors which should influence the selection of any given method for general adoption in technical laboratories are without doubt the accuracy of the results that can be obtained by its use, together with the time involved in its execution. When it is borne in mind that the technical chemist is daily confronted with a large number of determinations that are to be made, and that not only are metallurgical calculations, but also treatment charges on ores dependent on his results, the desirability of having simple, quick, and correct analytical methods is made apparent.

Without at all disparaging the methods employed by Messrs. Page, Hawkins, and Knight, it seems to the committee that the method described by Messrs. von Schulz and Low approximates more nearly to the conditions prescribed than do any of the others. It will be noted that the results given by Messrs. von Schulz and Low are comparatively high only in their determinations on samples Nos. 5 and 9, and attention is directed to the fact that in both of these samples the presence of cadmium is noted by Mr. Eakins, sample No. 5 containing the larger quantity. It is to be regretted that Mr. Eakins did not furnish the exact amount of cadmium contained,[*] but his results on this element were not requested by the committee, at the time the ores were submitted to him for zinc analysis.

The committee feels that the ores on which the investigations were made were such as have subjected the methods employed in the determination of zinc to a severe test. It is also aware that any method which would commend itself for general introduction must not only be a satisfactory one in the hands of its originators, but that it must also be capable of yielding concordant results when operated by others. This can only be determined by a fair and impartial trial.

If the inducements pertaining to von Schulz and Low's zinc method seem sufficient to warrant other chemists in investigating its merits, the committee will be glad to aid such in furnishing requisite material; and it will no less be pleased to publish such criticism as may be offered, if weaknesses in the method which are not now apparent are thereby disclosed.

E. N. Hawkins,
F. C. Knight,
L. J. W. Jones,
Henry E. Wood,
F. Guiterman,
*Committee.*

Addendum.—The following corrections from von Schulz and Low were received too late for insertion in the proper place:—After the word "solution," p. 6, col. 1, line 6 from bottom, add the following:—Owing to the fact that ores rich in sulphur occasionally react too violently by this treatment, it is best to vary the method in such cases by first adding 5 c.c. strong nitric acid to the ore, and heating in a covered casserole until the mass begins to become pasty, and then remove from the heat and add 20 c.c. of the chlorate solution and finish the evaporation as usual.

"Uranium acetate," p. 6, col. 1, line 35 from bottom, and col. 2, lines 19 and 26 from bottom, should read "uranium nitrate."

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Extra Meeting, December 13th, 1892.*

Mr. W. Crookes, F.R.S., Vice-President, in the Chair.

### *Stas Memorial Lecture.*

In opening the proceedings, the Chairman said:—"We are met to-night at an Extraordinary Meeting to do honour to the memory of one of the greatest chemists of this century, I might almost say one of the greatest chemists ever known to the world. This day is the first anniversary of his death, and it is a very happy thought on the part of the Council of the Chemical Society to hold a meeting on the occasion, in order that you may hear an account given of his labours. I had the very great advantage of being, I might say, a personal friend of Stas. I have been in his laboratory and seen his arrangements and apparatus, and there witnessed, among other things, a large mass of chloride of potassium, which took him years to prepare, with which he had made the most refined experiments, without detecting the slightest trace of sodium. I think that fact alone a most wonderful evidence of his marvellous skill."

Dr. Armstrong said, before reading the paper, he desired to state that it was a matter of great regret that it was impossible for Professor Mallet to be present. The Society were none the less much indebted to him, not only for having done what was asked of him, but more particularly for the example he had set. Last year, when a discussion arose as to the steps to be taken to secure appropriate notices of their eminent deceased foreign members, Stas and Kopp, the suggestion was made that it would be very desirable to take advantage of these and similar opportunities, not merely to give accounts of the work that our foreign members had done, but inasmuch as the foreign members are always men of great distinction and, as a rule, moreover, men who have lived a considerable number of years after they have accomplished their life work, that such notices, should, as far as possible, take the form of critical monographs of the subjects with which they have principally dealt. It seemed that in this way the Society would be doing educational work of very considerable service to its Fellows and to chemists generally. The matter was presented to Professor Mallet in this light, and there could be no doubt that he had responded in the most liberal manner possible to the appeal made to him; moreover, it was he who had suggested that a special meeting should be held on the anniversary of Stas' death. The delivery that evening of the first memorial lecture, therefore, was a very important step in the Society's history. It had been arranged that the work of Kopp should be dealt with in a similar spirit by the Treasurer, Professor Thorpe, in February next, on the anniversary of Kopp's death. Furthermore, it was proposed—and he hoped that in May next the proposal would be carried into execution—that, in like manner, on the anniversary of his death, the work of Von Hofmann should be commemorated. At present the plan was not fully developed, but it was somewhat as follows:—In order to deal with the subject from an English point of view, as our German *confrères* in Berlin were also engaged in the preparation of a similar account, it was proposed that Lord Playfair, who was intimately associated in early days with chemical science in this country, should recount his recollections of the state of chemistry at and prior to the time of Hofmann's arrival in England; that Sir Fredk. Abel should follow with an account of the work done at the Royal College of Chemistry under Hofmann, compiling this with the assistance of the remaining friends and pupils of Hofmann; and that the rise and progress of the coal-tar colour industry and its connection with the Hofmann

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[*] Mr. Guiterman, the Secretary of the Society, writes that Mr. Eakins has found 0 60 per cent cadmium in No. 5, and 0·15 per cent in No. 9. These amounts deducted from the results of the other chemists will give a better comparison with Mr. Eakins' on the samples in which cadmium was present.

school should be sketched by Dr. Perkin, who, he was glad to say, had consented to make his contribution to a large extent autobiographical. Whether it would be possible also to include in this memorial notice an analysis of the chief chemical work of Hofmann was not yet decided, this task being one of no slight difficulty and magnitude.

The following paper was read:—

81. "*Jean Servais Stas and the Measurement of the Relative Masses of the Atoms of the Chemical Elements.*" By J. W. Mallet.

The story of the life of Stas is first briefly told, and reference is then made to his researches in other directions than that of his specially chosen investigation of atomic weights; in order to fairly consider the contributions to knowledge in this latter direction which we owe to Stas, Professor Mallet next notices the succession of fundamental ideas which have gradually led up to the question, What is the mass of an atom of a particular element? This historical survey is followed by a lengthy section on the early history of investigations as to the atomic weights of the elements up to the year 1820; after which, reference is made to the determinations carried out from the time of Berzelius to that of Stas, a list, in chronological order, of the various published investigations being given.

Stas's work is then considered, the nature of the several general questions of fundamental importance in regard to matter as studied by the chemist, which he endeavoured to settle, being pointed out. These general questions are as follows:—

1. Is the mass or weight of an atom of a given element an absolutely constant quantity, so that chemical analysis, properly conducted, must always produce, from each substance examined, strictly the same relative quantities of the same constituents separated?

2. Assuming that the atomic weights of the various elements are severally fixed and immutable, are they represented by numbers which are commensurable, *i.e.*, are the atomic weights of all the other elements integer multiples of that of hydrogen?

3. If we assume the atomic weights of the elements to have constant values and to be represented by commensurable numbers, does not this indicate that all or most of the elements are, in reality, compound forms of matter—that, in short, we are as much called on to believe in the unity and unlimited interconvertibility of matter as in the unity and interconvertibility of energy?

4. Do experiments with substances raised to extremely high temperatures justify the belief that the elements may be dissociated into simpler forms of matter?

The rigour with which Stas investigated the methods of analysis, and the requirements he discovered and applied with a degree of patience and skill never before used in chemical investigation having been somewhat fully referred to, attention is directed to the results arrived at in the course of his elaborate researches.

The titles of his memoirs are given, together with a very lengthy list of the works and papers of other authors dealing with atomic weight determinations.

Professor Mallet then discusses, at considerable length, the objects to be aimed at, and the methods to be pursued in future investigations.

1. Attention is directed to the fact that Stas himself expressed the earnest wish that some other chemist, of sufficiently well established scientific authority, would take the trouble to check, by repetition, some one, at least, of his fundamental results.

2. It is eminently desirable that the work which Stas did for a few of the elements be extended to the entire list of those known—to rare as well as to common elements.

3. Certain of the elements particularly call for a more searching and exact investigation of their atomic weights—tellurium is a prominent example; cobalt and mercury are others; of these, the former may be expected to have a weight intermediate between those of iron and nickel.

4. It is desirable, then, in cases, such as that of iron, for example, in which the accepted value has been determined by study of a single change, should also be determined by other and independent methods.

5. It is eminently desirable that an attempt be made to directly determine the ratio between the atomic weight of hydrogen and that of each of the halogens, without in any way bringing in the atomic weight of oxygen.

6. The uncertainty as regards the elements of the yttrium group, and, in a less degree, those of the didymium group, requires clearing up.

7. It would be well to submit to experiment, by means as refined as those employed by Stas, the question of the absolute exactness of the well known law of "multiples."

8. Further enquiry into the close approach of so many atomic weights to the integer multiples called for by Prout's hypothesis is required.

9. It is necessary that the apparent periodic relationships among the elements should be discussed not merely, as heretofore, with the aid of roughly approximate atomic weights, but with exact weights, and, therefore, that more precise determinations of the numbers we would discuss should be made.

In the final section of the paper, the methods which it is desirable shall be pursued in the determination of atomic weights are discussed in detail, under the following heads:—

1. Selection of analytical or synthetical processes.
2. Use of pure materials.
3. Vigilance in regard to extraneous or accidental causes of error.
4. Choice as to the quantities of materials to be used.
5. Practical precautions as to accuracy in manipulation.
6. Precautions in regard to weighings.
7. Measurements by volume of liquids or gases.
8. Calculation of results.
9. Advantage to be derived from the application of greater working force and ampler means than can be commanded by private individuals to the determination of atomic weights. In this section, Professor Mallet advocates the establishment of a laboratory in which a small corps of competent chemists should be engaged solely in revising the whole list of atomic weights, with every precaution that could be devised to secure accuracy.
10. Final form of statement of results. In this section, it is argued at length that all atomic masses should be expressed in terms of the mass of the hydrogen atom taken as unity. The adoption of any other basis tends to confuse the consideration of any natural relations between these constants, as has been pointed out by Stas himself in reference to the hypothesis of Prout; numbers which, on the basis of $O = 16$, come very near to integers, cease to do so when H is taken as unity, and O has its true value, as determined by experiment, assigned to it.

The paper will occupy fully 60 pages in the Society's *Transactions.*

The Chairman, in proposing that hearty and sincere thanks be given to Professor Mallet for his paper, said the suggestions he had made were most valuable, and it was to be hoped they would stimulate the younger chemists to carry out investigations such as he had referred to. He could not help feeling that Stas was more honoured among the English-speaking races than on the Continent. On the occasion of his lamented death, twelve months ago, the scientific societies of Belgium petitioned the Government to purchase his apparatus and some of his pure materials, and, as many of his works could not be purchased, either because they were out of print or had been published in an inaccessible form, that funds should be voted for the publication of a complete set of Stas's memoirs and papers. After a considerable delay, the answer of the Government was to the effect that the schools were sufficiently supplied with apparatus and preparations. There was one memoir that Stas wrote that would be most valuable if it could be published, but he heard it was locked up in a Government Department. Stas was employed by the Government to investigate and determine the suitability of alloys of iron and other metals for the manufacture of heavy ordnance; his researches on the subject were most valuable, and he obtained some most important results; but hitherto all applications for permission to peruse his reports have been met with a refusal. If they could be made public, they would undoubtedly be of great value, both scientifically and practically.

Dr. RUSSELL said that about twenty-five years ago, when working on the atomic weights of nickel and cobalt, he had the pleasure of seeing Stas in London, who took a very considerable interest in this work; at that time he had met with certain difficulties in purifying nickel: Stas took considerable interest in the matter, and wrote out for him a paper of instructions recommending him to follow a certain course, and, only a month or so ago, he happened to come across this.

Professor DEWAR said that he was sure all must agree that one of the greatest services that could be rendered to the memory of Stas would be the complete publication of his memoirs. Resident as he had been in Belgium during a very interesting period of chemical history, he knew something of the support Stas gave to what, at the time, was a most revolutionary addition to chemical science. All present were aware that Kekulé was Professor in Ghent during many years, and the speaker was sure that he would be the first to acknowledge that it was largely owing to Stas's influence and assistance as an authority in Belgium, not only as a scientific man, but as a member of the highest social and political circles, that he was so splendidly supported by the Belgian Government. Furthermore, when the early memoirs of Körner, that are now classic, in which he suggested the position theory as an addition to the benzene or ring theory of Kekulé, were first submitted to the Belgian Academy, it was really Stas who secured their publication, and it was his encouragement of Körner's work that promoted the advent of the position theory in organic chemistry. To touch on the vast work of his life, and to attempt to criticise his researches, makes an ordinary observer feel exceedingly small. He always felt that, in comparison with modern work, a paper by Stas was an oasis of intellectual fruitfulness in a desert of arid vapid publication. We were all alike; we were all equally to blame; at home and abroad there was the same general tendency: the result being that our scientific literature is burdened by too many trivial, common-place productions, exhibiting no trace of any desire to cultivate originality or thoroughness. No chemist could read a paper by Stas without feeling himself an exceedingly small man. The noble inheritance left by Stas to chemists must live for ever, and it will always be a pleasure to any chemist wishing to cultivate his higher faculties, to read and study, and attempt to imitate his works.

Professor DEWAR then referred to the determinations of the atomic weight of manganese and of the molecular weight of triethylamine, which he had carried out in conjunction with Dr. Scott (*cf. Proc. Roy. Soc.*, 1883, 35, 44, 347). We were greatly indebted to Professor Mallet for the admirable *résumé* he had given, and for his friendly and critical remarks. He also, said Professor Dewar, was of opinion that the near approach in quite a number of the atomic weights to whole numbers is still a matter of very serious suggestive interest, and he proceeded to call attention to the results obtained on taking into account the values that the late Professor Dittmar found for the oxygen and hydrogen ratio, remarking that no man more competent to deal with this subject could be found, and that all must deeply deplore his loss while engaged in doing such splendid work on the very question under discussion. If we accepted Dittmar's number, which is corroborated by nearly half a dozen separate researches, 15·87, as expressing the ratio between the atomic mass of oxygen and the atomic mass of hydrogen, it appeared that the best-determined atomic weights fall into two totally different categories; some that apparently could not possibly be regarded as multiples of that of hydrogen approaching nearer, while others, seemingly very near to, are now far from being multiples of the atomic weight of hydrogen. Thus, silver, taking the Dittmar ratio, would come out very nearly a whole number, viz., 107·046. The most recent determinations of copper would give the value 63·09. Tin would be within 0·1 of a unit. In the same way, antimony would be within 0·1. Iodine, however, would be out. Zinc, also, would be decidedly out. Beryllium would be nearly a whole number. Bromine would be 0·26 out. There could be no doubt that in the case of gold the number would be 195·61; while platinum would be 193·28, cerium 139·06, and boron 10·87, or near that. Professor Mallet made reference in his paper, he believed, to chlorine as an element which no one anticipated would come nearer a whole number than half a unit; but, as a matter of fact, chlorine now came within 0·2, viz., 35·16 of this element, and would fall into the class nearly approaching whole numbers. He noticed that Mallet had adopted the latest value of nitrogen. In his 1865 paper, the value 14·045 was given by Stas as the result of a very large number of determinations. Prof. Dewar said he believed the number 14·055 was deduced entirely from experiments on the synthesis of nitrate of silver. Stas was so conscientious that he altered the value from 14·045 in his later paper in 1875, he believed, because the weight of nitrate of silver obtained by synthesis before fusion differed very slightly from the weight after fusion, and he thought that it was not fair to depend on the weight after fusion, because there might be a slight loss of nitric acid. Consequently, in his later paper, he adopted 14·055, but that number is the result only of two determinations of the synthesis of nitrate of silver, whereas in 1865 there were ten or twelve different reactions from which the atomic weight of nitrogen was shown to be 14·045, not 14·055. This led him to remark that if we took the weight of ammonium as directly determined, which is probably as accurate a weight as any of Stas's numbers, viz., 18·076, and deducted 14·045 from it, the atomic weight of hydrogen relatively to 107·9 of silver or 16 of oxygen was 1·0077. That would give a ratio of the atomic weights of hydrogen to oxygen, transforming hydrogen to unity, of 1 to 15·88, so that Stas's determination of the weight of ammonium, deducting his own value for nitrogen, gives the ratio of the atomic weight of hydrogen to oxygen found by Dittmar, Rayleigh, and all the more recent investigators. He did not say this result is a coincidence; it must be due to the accuracy with which Stas determined the separate atomic weights. It was interesting to observe that the most recent density determinations gave both nitrogen and oxygen a little too high from the gravimetric point of view. Thus the determinations of Leduc make nitrogen and oxygen respectively 13·99 and 15·9, instead of 13·93 and 15·87; this was what we should expect if the oxygen, as we believe, be a little too dense, being nearer its critical point than hydrogen is, and the same applies to nitrogen. He could not help thinking the proposal made by Prof. Mallet, that the determination of atomic weights should be given to a Board, would not turn out quite satisfactory in practice. But there were many points all would wish to clear up, and it would be a noble piece of work for some one to follow out Stas's own work, namely, to repeat any one of his fundamental syntheses. It would require a man of the type of Dittmar to do such work, however. Dittmar had, in fact, attempted the re-determination of one of Stas's values, and it was very important that we should have an explanation of the difference between the two workers. Dittmar had found in the case of lithium a number something like 6·85, whereas Stas's value was 7·02. Dittmar's method involved the analysis of lithium carbonate. He also determined the value of sodium by a similar method, and obtained absolutely the same value as Stas for sodium. What was the explanation of such a remarkable difference in the value found by the Stas method? In the case of cadmium, also, there was apparently a difference of half a unit between some of the determinations. What was the reason of these differences? He referred to such cases as these two of lithium and cadmium, but there were others, and the problem was to find out how it is that methods nearly equally accurate, but differing essentially, give such discordant results, the work being carried out with the accuracy nowadays attainable. Finally, he was very glad to have had the opportunity of expressing his grateful thanks for the kindness of Stas in the past, and of bearing testimony to the great service he had done to science.

Dr. Scott referred to the work on which he was engaged in connection with Lord Rayleigh, with the object of determining the densities of oxygen and hydrogen, he having undertaken the determination of the volume ratios. Latterly, he had prepared hydrogen by passing steam into sodium, condensing it in palladium, and had obtained oxygen from oxide of silver; the experiments were made with successive fractions of the two gases driven off from the solid materials, which were kept in vacuous chambers sealed on to the gas analysis apparatus. He had now succeeded in obtaining the oxygen and hydrogen so pure that from the first fraction to the last he could detect no difference between them in the last series of determinations; whereas on using the hydrogen directly prepared from sodium and steam, the ratio was 1 to 2·00243, that calculated on the whole of the hydrogen separated from the palladium was 2·00245. The last two figures he could hardly depend on.

Dr. Bailey thought that the extraordinary care taken by Stas in preparing and examining his materials, and in studying the changes made use of in his atomic weight determinations, served perhaps more than anything else to impress the student of his works. Referring to his own work, he mentioned having noticed that materials which are generally regarded as stable and non-volatile may be carried off by steam when their solutions are slowly boiled. Was it not conceivable that potassium chloride might thus be carried off in quantity sufficient to influence an atomic weight determination? He next spoke of the difficulty of obtaining concordant results in determining chlorine in the compounds of platinum metals. How this arose he was not able to say, but other workers had met with similar difficulties.

In closing the discussion the Chairman expressed agreement with previous speakers that atomic weight determinations could not well be carried out by an organisation such as Professor Mallet had suggested.

## NOTICES OF BOOKS.

*The Microscope: Its Construction and Management.* Including Technique, Photo-micrography, and the Past and Future of the Microscope. By Henri Van Heurck, Professor of Botany and Director at the Antwerp Botanical Gardens; late President of the Belgian Microscopical Society, Hon. F.R.M.S. and New York M.S. English edition. Re-edited and augmented by the Author from the fourth French edition, and translated by Wynne E. Baxter, F.R.M.S., F.G.S. London: Crosby Lockwood and Son. New York: D. Van Nostrand Company, 1893. Large 8vo., pp. 382, with three Plates and upwards of 250 Illustrations.

Standard works on the microscope, its manipulation, and its application, are not too numerous in our literature, and without any disparagement to the writings of Dr. Beal, of Carpenter, and Quekett, we can give the present volume a most hearty welcome. It is written by a thoroughly competent authority, and is fully on a level with the most recent improvements both in the construction of the instrument and in its management.

After an introductory chapter on elementary optics we find an account of Prof. Abbe's theory of microscopical vision, and a series of experiments on the application of this theory due to Mr. J. W. Stephenson and laid before the Royal Microscopical Society of London by Mr. F. W. Stephenson.

In Book I., Chapter I., the author enters upon the microscope generally, passing on to a detailed examination of its parts. Here we regret to notice a defect of the book. The figures are duly lettered, but there follows no complete reference to the lettering, so that the figure is in some cases useless. Objectives and tests are very clearly described. Stages, movements, diaphragms, and condensers come next under review, the references to the lettering being still very deficient. This is particularly to be regretted in case of the Abbe condenser (Fig. 70).

Under accessory apparatus we have an account of the microspectroscopes of Sorby and Zeiss, the figures of the latter instrument lettered, indeed, but without explanation. As an illuminant, in default of daylight the author uses a petroleum lamp, or the electric glow-light, where available. Like all practical authorities he recommends that the windows of the work-room should face the north or the north-west. M. Van Heurck does not consider that microscopic research, if properly conducted, is injurious to the eyes. On this subject he gives some very judicious advice.

A very important part of the work is devoted to the compound microscopes of the best makers, the peculiarities of the various models being carefully described, and the instruments themselves are figured. In many cases there is a tabular account of the objectives furnished by the principal firms, giving the equivalent focus, the numerical aperture, and the price of each. It will be remarked that the production of apochromatic objectives is not now confined to the firm of Zeiss and Co., of Jena.

Among the makers Messrs. Powell and Lealand meet with high, and we believe fully merited, praise. It is said that their instruments are used in England by all "*serious* microscopists." This epithet is a gallicism which will call up a smile. Watson and Sons, who carry out certain specifications of the authors, are highly praised and have carried off high honours at the recent Micrographic Exhibition. The firm of Carl Zeiss, of Jena, is, however, characterised as the most important in the world.

Photo-micrography is expounded at great length in Book III., Chapter II.

A very important section treats of the cause of errors in microscopical observations, such as iridescence and diffraction, *Muscæ volitantes*, astigmatism, and dust on the glasses. After some useful remarks on the preservation of the glasses, the author proceeds to give instructions for preparing objects. In preference to Canada balsam he recommends storax and liquid amber, which have the advantage of not darkening on long preservation.

The arsenical medium of H. L. Smith, realgar, dissolved in arsenic bromide, the author obtains by melting together in a retort 1 part of sulphur and 1·7 part of arsenious acid heated to the distilling point. A caution is given concerning the dangerous vapours. In a subsequent formula 30 parts flower of sulphur are dissolved in 10 parts bromine, and the whole is heated with 13 parts of pure arsenic in fine powder, and heated until a drop taken out and cooled becomes very brittle.

An interesting chapter entitled "The Microscope in the Past and the Future," gives a history of this instrument and suggestions as to its future development. In fine, Dr. Van Heurck's work must be pronounced a boon to all English readers interested in microscopy.

We regret that the translator has repeatedly used the term "Marie-bath" in place of the recognised and intelligible English word water-bath. "Bain-marie" is a survival of ignorance and superstition to which the French still cling, but there is no excuse for the attempt to introduce it in English writing.

The index is admirable, and the entire getting up of the book reflects the greatest credit on the publishers.

## CORRESPONDENCE.

### DISINFECTANTS—AN EXPLANATION.

*To the Editor of the Chemical News.*

Sir,—Dr. Klein's rejoinder calls for an answer. I have already shown that in his first letter (I mean the one in which periodate crystals were erroneously quoted with "aminol") certain statements were partly incorrect, partly misleading. I now confine myself to such matters as have not been touched upon in my previous letter.

I again quote from Dr. Klein's report: "This solution (1 in 600) is in itself a perfectly harmless fluid as regards the human organism; therefore, when applied to wounds, no undesirable disturbances could ensue owing to its being absorbed. This is well known to be the case with some antiseptics, as in carbolic acid applications, or in the use of perchloride of mercury."

And now I shall quote from "Koch, on Disinfection," abstracted and translated by Whitelegge, published by the New Sydenham Society.

(1) "For practical purposes a disinfectant should not require much longer than twenty-four hours."

(2) "Except chlorine, bromine, and iodine, only mercuric chloride, osmic acid, and potassic permanganate (5 per cent) destroyed anthrax spores within twenty-four hours. Since a 5 per cent solution of permanganate is inadmissible for disinfection in bulk, and osmic acid is out of the question, we have left only mercuric chloride and iodine, bromine, and chlorine."

The strength in which the above-named substances succeeded in destroying anthrax spores in twenty-four hours are stated in Koch's tables, thus:—

| | | | | | |
|---|---|---|---|---|---|
| Permanganate aqueous solution | | .. | 5 | per cent | (1 in 20) |
| Bromine | " " | .. | 2 | " | (1 in 50) |
| Chlorine | " " | .. | ? | | |
| Iodine | " " | .. | ? | | |
| Mercuric chloride | " " | .. | 1 | " | (1 in 100) |
| Osmic acid | " " | .. | 1 | " | " |

Now put against these declarations and records of Koch's the fact that Dr. Klein found "aminol" (strength 1 in 600), which he himself calls a perfectly harmless fluid, kills 94 per cent of the spores of anthrax in twenty-four hours, and its claim to be classed amongst true disinfectants is too obvious to be gainsaid.

That the designation "a true disinfectant" is meant by me to apply only to such strengths of solutions of "aminol" as have the power of destroying anthrax spores in twenty-four hours or thereabout, Dr. Klein may rest assured, as also that nothing has been or will be done by me intentionally to commit him to anything which is not fully warranted by his results as recorded in his authorised published report.—I am, &c.,

Hugo Wollheim.

101, Leadenhall Street, London, E.C.,
January 4, 1893.

### THE POSITION OF CHEMISTS.

*To the Editor of the Chemical News.*

Sir,—The letters of your correspondents, Mr. T. H. Davies and "Dare Lucem," again open the question of the position of the Institute of Chemistry and of chemists in relation to it. It must be admitted that the Institute made no really satisfactory progress until within the last year or two, when signs of some sort of improvement were shown by the fact that the examinations were conducted upon approximately reasonable lines. The position of the Institute up to the present, in the opinion of a large section of its members, has been unsatisfactory for the reason that a constant majority of the Council has consisted of Fellows more interested in teaching than in the practice of Consulting and Analytical Chemistry, and it is evident that the proper step to take in order that progress may be made is to reverse this condition of things by electing as Members of Council a majority of Fellows who are Consulting and Analytical Chemists either in active general practice or in connection with Works, or who are concerned with special technical processes.

The knowledge and experience required by persons acting as Consulting and Analytical Chemists is very different from that required for teaching chemistry. It is well known that some lecturers and teachers do not appreciate the extent of that knowledge and experience required for the professional work referred to. It seems curious, therefore, that the Council of the Institute should be composed chiefly of those who do not belong to the class of members (by far the largest) for whose benefit the Institute was specially founded. The Institute of Chemistry Reform Association desires to obtain an alteration in this respect at the next election, and I would venture to suggest through your columns that chemists engaged in general practice, or who are more concerned with the duty of acting as advisers to the public or to private individuals than with that of teaching students, should endeavour to bring about the necessary change in the constitution of the Council.

We are perfectly cognisant of the valuable services to the Institute which have been rendered by many eminent professors of chemistry, and we have not the least desire to lose the advantage of their guidance and even in many respects of their control; but we feel sure that it is only reasonable to ask that the majority of those on the Council should consist of members for whose advantage the Institute was specially founded.

As a preliminary step we are suggesting the names of three Fellows of the Institute who are more interested in Consulting and Analytical Chemistry than in teaching for election as members of Council, and I shall be glad to supply forms to any member of the Institute who has not as yet signed a nomination form, and who may be willing to support any one of the three suggested candidates.—I am, &c.,

William Thomson,
Hon. Sec. to the Institute of Chemistry
Reform Association.

Royal Institution Laboratory Manchester,
January 5, 1893.

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—In common, no doubt, with other Fellows of the Institute of Chemistry, I have this morning received a circular from a body calling itself the "Institute of Chemistry Reform Association," signed by Mr. Wm. Thomson, as hon. sec., in which I am asked to inform the Committee whether I will or will not support them in their endeavours to transform the minority of analytical chemists on the Council into a majority.

I shall be grateful if you will afford me space in which to give my reasons for not thinking that such a change would be advantageous to the body of Fellows and Associates forming the Institute.

I take it that, as its name implies, the Institute is intended to exist for the benefit of all who are chemists and not of analytical chemists only, which seems to be admitted by the Committee of the Reform Association, as in their circular they "appreciate the valuable services rendered to the Institute by eminent professors of chemistry, and desire to retain many of them on the Council, but . . ." In fact, they think there are too many of them!

Now, sir, as one of the functions of the Council is to ascertain the fitness of those who present themselves as candidates for admission to the Institute, it is of vital importance that no action should be taken which would in any way have the effect of lowering the standard of admission. But this, I fear, would be the result of having a preponderance of analytical chemists upon the Council.

Without in the least implying that the three gentlemen for whom we are asked to vote are not fit and proper persons to be nominated, it is highly probable that a majority of analytical chemists would take a less broad view of the education necessary for membership than a majority of professors.

Analytical chemists tend to become specialists, and in the routine work of their profession there is little time for them to make themselves acquainted with the work done in other branches of knowledge, scientific or literary. Professors, on the other hand, have far better opportunities of knowing what is being done both in chemistry and in other subjects, for, in the former they are obliged in the course of their ordinary vocation to revise periodically their knowledge of the subject, and as to other subjects the nature of their work gives them more abundant leisure than any analytical chemist in good practice can have.

It is the practice in the laboratories of many analytical chemists to take pupils and to train them by giving them the ordinary analytical work of the laboratory to do. I will not dwell either upon the morality of sending results to clients which have been obtained by inexperienced pupils, nor upon the cutting down of fees by the employment of such pupils, although such action is the cause of the discontent at present existing in regard to the Institute. But if analytical chemists were to become a majority on the Council, there is little doubt that the first action taken would be to make the record of the work done by a candidate in an analytical laboratory a principal element in the admission examination. To those who know how, in too many cases, such pupils are suffered to pick up their knowledge, and who recognise the limited nature of the instruction to be obtained in the majority of professional laboratories, the prospect of such action is not re-assuring.

It is because I believe that if the Reform Association should carry its nominees, the value of the title of Fellow will become degraded, that I, a practising analytical chemist, decline to assist the Committee in their endeavour, and not because I have anything to say against their nominees personally.—I am, &c.,

R. W. Atkinson.

Cardiff, January 10, 1893.

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**Royal Institution.**—On Tuesday next (Jan. 17), Prof. Victor Horsley, F.R.S., will begin a course of ten lectures on "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology." On Thursday (Jan. 19), the Rev. Canon Ainger will begin a course of three lectures on "Tennyson," and on Saturday (Jan. 21), Dr. C. Hubert H. Parry will begin a course of four lectures on "Expression and Design in Music" (with Musical Illustrations). The Friday Evening Meetings will begin on Jan. 20, when Prof. Dewar will give a discourse on "Liquid Atmospheric Air."

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxv., No. 24, December 12, 1892.

**The Rise of Temperature under the Influence of Injections of Soluble Microbian Products.**—MM. Bouchard and Charrin.—The authors discuss the increase of animal heat produced by the injection of microbian liquids, even if previously filtered.

**Temperature of the Electric Arc.**—J. Violle.—The author has experimented upon the electric arc as obtained under a great range of conditions. He finds that the hottest part of the positive carbon and of the arc has a temperature of 3500°, which is the heat at which carbon is volatilised.

**The Magnetic Properties of Oxygen at Different Temperatures.**—P. Curie.—This paper requires the two accompanying figures.

**The Fusion of Calcium Carbonate.**—A. Joannis.—The author is of opinion that calcium carbonate cannot be fused without the aid of extraneous pressure except at temperatures notably exceeding the melting-point of gold.

**Ammoniacal Compounds derived from Ruthenium Sesquichloride.**—A. Joly.—The limited action of water upon the ammoniacal chloride produces a liquid of an intense violet-red colour. If the anhydrous chloride in a state of fine division is projected into an ammoniacal solution saturated at a very low temperature and allowed to digest for some time, the deep red liquid obtained deposits small brown crystalline laminæ,—

$$Ru_2(OH)_2Cl_4(NH_3)_7+3H_2O.$$

The solution of this salt is red by transmitted, but violet by reflected light. Its tinctorial power is comparable to that of the most intense organic colouring-matters. A solution at 1·100000th transmits only the red and orange rays. A solution at 1·5000000 is still of a distinct rose colour. If the solution is boiled it is rapidly destroyed, but it yields intermediate products, violet red, violet black, and, lastly, black.

**A Phosphorus Iodosulphide.**—L. Ouvrard.—This compound may be obtained by dissolving in carbon disulphide quantities of sulphur, phosphorus, and iodine, corresponding to the formula $P_2S_3I$. It forms brilliant crystals of a golden yellow, permanent in dry air, but slowly attacked by moist air with an escape of hydrogen sulphide. It is very soluble in carbon disulphide, sparingly soluble in benzene and chloroform, and still less soluble in ether and absolute alcohol.

**Action of Bismuth upon Hydrochloric Acid.**—A. Ditte and R. Metzner.—Like antimony, bismuth is not affected by hydrochloric acid if every trace of oxygen is excluded. If oxygen is present, a corresponding quantity of the metal is dissolved.

**The Action of Potassa and Soda upon Antimony Oxide.**—H. Cormimboeuf.—In the moist way, soda acting upon amorphous antimony oxide forms sesquibi- or tri-antimonites, whilst potassa produces a tri-antimonite alone.

**The Relation between Formation-Heats and the Temperatures of the Point of Reaction.**—Maurice Prud'homme.—For one and the same series of substances the formation-heat of the unit of mass is proportional to the specific heat, and inversely as the absolute temperature of the point of reaction.

**Study of the Chemical Reactions in a Liquid Mass by the Index of Refraction.**—C. Féry.—This memoir requires the accompanying diagram and table.

**A Propylamidophenol and its Acetylic Derivatives.**—P. Cazeneuve.—Propylamidophenol in an alkaline solution is a powerful photographic developing agent. According to M. Lumière, this power is found in aromatic substances, having at least two phenolic OH, or one $NH_2$ and one OH group, and that these two groupings must be in the *ortho-* or *para*-position. The *meta*-position yields only indifferent substances. Thus pure resorcine does not develop, whilst pyrocatechine and hydroquinone develop.

**Determination of Impurities in Methylenes.**—Er. Barillot.—(See p. 15).

**Separation of Micro-organisms by Centrifugal Force.**—R. Lezé.—(See p. 15).

**Losses of Ammonia in Farm-yard Manure.**—A. Muntz and A. Ch. Girard.—The observations of the authors show that the losses of ammonia chiefly take place in the stables, and that abundance of litter is no remedy.

**The Fermentations of Dung.**—Alex. Hébert.—The losses of nitrogen from farm-yard manure kept duly moist do not take place in the state of ammonia. Hence the addition of ferrous sulphate, of gypsum, or sulphuric acid is not of much use.

### *Bulletin de la Société Chimique de Paris.*

Series 3, Vols. vii. and viii., No. 23.

**Utilisation of Burnt Pyrites for the Manufacture of Salts of Iron.**—A. and P. Buisine.—The author treats the finely pulverised pyrites with sulphuric acid of from 50° to 66° B., using a temperature not exceeding 300°. At this heat the authors obtain a sulphate which is slightly basic, and which they propose as a substitute for ferrous sulphate, in agriculture, in the purification of coal-gas, as a disinfectant, &c.

**Purification of Sewage with Ferric Sulphate.**—A. and P. Buisine.—The authors show that it is possible in this manner to purify continuously large volumes of sewage. They consider that for this purpose it is superior to lime, which is self evident. They propose to extract the fatty matters from the precipitate by means of carbon disulphide, and to use the rest of the organic matter as a manure, which is said to contain 3 per cent of nitrogen.

**Condensation of the Aldehyds of the Fatty Series with Cyanacetic Acid.**—M. Fiquet.—Not adapted for useful abridgment.

**Rotatory Power of Fibroine.**—Leo Vignon.—The matter precipitated by alcohol from the hydrochloric solutions of fibroine is identical with fibroine. It possesses the same weight, the same action upon polarised light, and behaves in the same manner with reagents and colouring-matters.

**New Preparation of Acetylene.**—L. Maquenne.—Barium carbonate is the only one of the alkaline-earthy compounds which is by degrees almost entirely transformed into a carbide under the influence of magnesium. Calcium carbonate is only very incompletely attacked, and gives then, if treated with water, a poorer mixture of hydrogen and of acetylene.

**The Preparation of Ethylene Periodide (Tetraiodethene).**—L. Maquenne.—The author obtains this compound by submitting acetylene to the action of iodine in an alkaline solution.

**Action of Ammonia and the Amines of the Fatty Series upon Acetylacetone.**—A. and C. Combes.—This extensive paper does not admit of useful abridgment.

**The Pyrogallol Antimonites.**—H. Causse and C. Bayard.—The authors describe the acid and the neutral compounds, and the behaviour of the latter with acetic anhydride and acetyl chloride.

**The Action of Diamines upon Acetylacetone.**—A. and C. Combes.—An extension of the former paper to the diamines.

**Detection of the Radicle Benzoyl in Organic Compounds.**—E. Leger.—For the detection of cocaine in toxicological analyses, Ferreira da Silva proposes a reaction characterised by the formation of odorous products easy to recognise. It consists in treating some m.grms. of cocaine, or of one of its salts, with fuming nitric acid at 1·4 specific gravity, evaporating to dryness in the water-bath and pouring upon the residue some drops of a concentrated alcoholic solution of potassa. There is then evolved a very distinct odour resembling that of peppermint. According to Béhal, the odoriferous principle is ethylbenzoate. M. Leger finds that the reaction is produced with other substances which, like cocaine, contain the radicle benzoyl.

**The Preparation and Properties of Fibroine.**—Leo Vignon.—The author takes a skein of clean white silk weighing about 10 grms., and treats it for thirty minutes at ebullition in a bath of 150 grms. neutral white soap and 1500 c.c. distilled water, turning it frequently. The silk is then wrung, rinsed with distilled water, first hot and then luke warm, to remove the soap. When drained it is submitted for twenty minutes to the action of a second boiling soap bath of the same composition as the former. It is then carefully drained, rinsed successively in 1 litre of boiling distilled water, 1 litre of luke-warm distilled water, 1 litre of cold distilled water containing 10 c.c. of pure hydrochloric acid at 22°. Lastly, it is again rinsed in distilled water and twice washed in alcohol at 90°. We thus obtain 75 per cent of silk very white, brilliant, supple, tenacious, and elastic, which must be regarded as true fibroine. Its specific gravity is 1·34. Its mean percentage composition is—

| | |
|---|---|
| C .. .. | 48·3 |
| H .. .. | 6·5 |
| N .. .. | 19·2 |
| O .. .. | 26·0 |
| | 100·0 |

The ash of silk is about 0·80 per cent, but that of fibroine is only 00·1. If dissolved in concentrated hydrochloric acid, fibroine is strong lævorotatory, $\alpha_{(i)} = -40°$.

No. 24.

**The Rotatory Power of Cyclic Bodies.**—Albert Colson.—The product of asymmetry, based upon the theory of asymmetric carbon, cannot generally indicate the direction of the deflection in bodies possessing a rotatory power; and the theory of asymmetric carbon is an incomplete presentation of the principle of dissymmetry, and cannot be accepted without reservations.

**On the Nature of Solutions.**—A. Reychler.—The author considers the dissolved substance when it is not and when it is an electrelyte, and then examines electrolysis itself.

**Certain Double Salts of Quinine.**—E. Grimaux.—An examination of quinine chlorhydrosulphate, bromhydrosulphate, and iodhydrosulphate.

**Ampelochroïc Acids.**—A. Gautier.—Each variety of *Vitis vinifera* produces one or more colouring-matters. All these colouring-matters, to which the author gives the name œnolic acids, possess feebly acid properties. If they are melted with caustic alkali they are split up into (1) phloroglucine, (2) aromatic acids generally, the protocatechuic or hydroprotocatechuic acids, (3) acids belonging to the fatty series or to the non-saturated series, $C_nH_{2n}-2O_2$ and $C_nH_{2n}-2O_3$. The author has distinguished in the coloured tannins or ampelochroïc acids three varieties, α, β, and γ. The colours of autumnal leaves cannot be ascribed to erythrophyll or to its modifications, but to phlobaphenes and catechines.

*Revue Universelle des Mines et de la Metallurgie.*
Vol. xix., No. 2, August, 1892.

**Silicon and Aluminium in the Metallurgy of Steel.**—Prof. Sergius Kern.—The author concludes that the best reductive addition for steel castings is silico-spiegel at 10 per cent of silicon and 12 per cent of manganese. After casting, the products ought to contain from 0·25 to 0·30 per cent of silicon. Mr. J. W. Spencer, manager of the Newburn Steel Works, made experiments to the same end, almost simultaneously with Prof. Kern, and arrived at results almost identical. Aluminium was found to be an excellent reducing agent, decomposing the oxides and giving a metal without blow-holes. But in castings of 165 to 250 kilos. it yields a crystalline structure which is very defective. In castings of small weight nearly 0·1 per cent of aluminium may be introduced. The presence of this metal increases the resistance to breakage.

**Determination of Sulphur in Fuel by the Eschka Process.**—Dr. Franz Hundeshagen.—From the *Chem. Zeitung.*

Series 3, Vol. xx., No. 2.

This issue contains no chemical matter.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. vii., No. 82.

**Report made by M. de Luines on Behalf of the Committee of Chemical Arts, on the Bleaching-Process of M. Hermite.**—The author obtains his bleaching agent by the electrolysis of a mixture of 1000 parts of water, sodium chloride 50 parts, and magnesium chloride 5 parts. Only the magnesium chloride and the water appear to be decomposed, forming at the positive pole a compound of great decolourising agency. There is no fear of the presence of free soda. The bleaching bath contains per litre from 0·5 grm. to 2 grms. per litre. An electrolyser of Hermite's system produces in twenty-four hours the equivalent of 100 kilos. dry chloride of lime at a cost of 5·22 francs, if hydraulic power is used; or 10·02 francs, if steam has to be employed.

## MEETINGS FOR THE WEEK.

MONDAY, 16th.—Medical, 8.30.
TUESDAY, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "Mexico, Past and Present," by Edward J. Howell.
WEDNESDAY, 18th.—Society of Arts, 8. "The Mining Industries of South Africa," by Bennett H. Brough, Assoc. R.S.M.
—— Meteorological, 7. (Anniversary).
—— Microscopical 8. (Anniversary).
THURSDAY, 19th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Tennyson," by the Rev. Canon Ainger, M.A., LL D.
—— Society of Arts, 4.30. "The Currency Problem," by J. Barr Robertson.
—— Chemical, 8. "The Determination of the Thermal Expansion of Liquids," by Prof. T. E. Thorpe, F.R.S. "The Thermal Expansion and Specific Volumes of Certain Paraffins and Paraffin Derivatives," by Prof. Thorpe, F.R.S., and Lionel M. Jones, B.Sc. "The Hydrocarbons Formed by Decomposition of the Citrene Dihydrochlorides," by W. A. Tilden, F.R.S., and Sidney Williamson. "Camphorosulphonic Derivatives," by F. S. Kipping and W. J. Pope. "Note on the Decaphanes Formed from Terpenes and Camphor," by Henry E. Armstrong.
FRIDAY, 20th.—Quekett Club, 8.
—— Royal Institution, 9. "Liquid Atmospheric Air," by Prof. Dewar, F.R.S.
—— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
SATURDAY, 21st.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Pipes for Corrosive Liquid.**—I should be much obliged if some correspondent would, through the medium of your paper, inform me what metal pipes could be used effectively for conveying strong (cold) solutions of corrosive sublimate?—W. G. KENT.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1730.

## ON THE ORIGIN OF COLOUR.

### I. Relation of Molecular and Atomic Volume to Colour.

By WILLIAM ACKROYD, F.I.C.,
Public Analyst for Halifax.

In the presence of an influx of new and old ideas regarding the origin of colour, I may be permitted to point out that some eighteen years ago I constructed a metachromatic scale, a generalisation resulting from the study of colour changing bodies, and I applied the scale to the study of colour in compounds, arriving at a law of colour for binary compounds (Chem. News, xxxiv., p. 76, and *Phil. Mag.*, Dec., 1876). In discussing the cause of these phenomena, I initiated the idea of "potentiality." The year after I published a method of making, and the measurements made, of the molecular aggregates concerned in these structural absorption phenomena (Chem. News, xxxvi., p. 159).

In 1884 Carnelley, using the metachromatic scale I had devised, and surveying the subject from the more comprehensive vantage ground of the periodic law of the elements, showed that there are indications that the colour of compounds is a periodic function of the atomic weight (*Phil. Mag.*, Aug., 1884). In the early part of 1892 I communicated to the Physical Society of London what I take to be the law of colour and constitution in a paper which is not yet published. The law may be thus briefly stated:—In a series of molecules with a constant radical R, and a weight-variable radical R′, the colour varies in a definite order, increase of weight of the variable radical R′ causing change of colour towards the black end of the colour scale (see below). In support examples were given in which R′ was an electro-negative element; elements belonging to a natural series like Mg, Zn, Cd, and Mg, combined with a common simple or compound radical; water in crystalline salts; an organic radical like $NH_2$, or a metal in an isomorphous group.

The following argument has occurred to me, which may be taken as a further contribution to this interesting subject. A colour-changing body has its temperature gradually raised and its colour altered in the order of the metachromatic scale; during this change its specific gravity is decreasing, and we may assume that inversely its molecular volume is increasing. Hence we may correlate the change of colour from white through the scale to black with increase of molecular volume, thus—

White, blue, green, yellow, orange, red, brown, black.

⟶

Increase of molecular volume.

A similar difference of molecular volume in comparable compounds exhibiting conformity with the laws of colour referred to in the first paragraph, is apparent in the following examples which I have calculated:—

*Pairs of Binary Compounds.*

| | Molecular volume. |
|---|---|
| $HgO$, red | 19·5 |
| $Hg_2O$, black | 43·4 |
| $Bi_2O_3$, yellow | 56·7 |
| $Bi_2O_5$, brown | 84·1 |
| $Sb_2O_3$, white | 49·9 |
| $Sb_2O_5$, yellow | 49·1 |

*Crystallised Salts.*

| | |
|---|---|
| $CuSO_4$, white | 44·0 |
| $CuSO_4,5H_2O$, blue | 113·0 |
| $PtCl_2$, green | 45·3 |
| $PtCl_4,8H_2O$, yellow | 196·7 |

*A Natural or Periodic Series of Compounds.*

| | |
|---|---|
| $MgO$, white | 11·8 |
| $ZnO$, white to yellow | 14·8 |
| $CdO$, red to brown | 15·6 |
| $HgO$, red | 19·5 |
| $ZnS$, white | 24·8 |
| $CdS$, yellow | 31·9 |
| $HgS$, white to black | 30·0 |

*An Isomorphous Group of Oxides.*

| | |
|---|---|
| $Al_2O_3$, white | 25·0 |
| $Cr_2O_3$, green | 30·3 |
| $Fe_2O_3$, yellowish red | 30·3 |

The coloured non-metallic elements also exhibit the same relations of colour to atomic volume, thus—

| | Atomic volume. |
|---|---|
| Sulphur, yellow | 31·2 |
| Selenium, red | 37·2 |
| Chlorine, green, liquid | 53·3 |
| Bromine, red, liquid | 53·9 |
| Iodine, dark red, liquid | 56·3 |

Carbon in its different forms conforms to the same law.

These examples from compounds and elements comparable among themselves therefore demonstrate a new law, viz., *that increase of absorption of light in the order of the metachromatic scale is accompanied by increase of molecular and atomic volume.*

At the present stage of the inquiry it is difficult to say what are real exceptions to this law on account of the uncertainty in some cases as to what may be the molecular weight of compounds which cannot be vapourised; thus cupric oxide with the formula $CuO$ would be an exception when compared with cuprous oxide, $Cu_2O$. Is the formula of cupric oxide, however, $CuO$ or $xCuO$? If we take it as $Cu_2O_2$, *e.g.*, it conforms to the law.

Halifax, Jan. 12, 1893.

## ON THE ANALYSIS OF FERROSILICON AND SILICEOUS SPIEGEL.

By T. W. HOGG.

The recent publication in the Chemical News of Zeigler's paper on the examination of ferro-alloys suggests that there are in use many unnecessarily complicated analytical processes.

Amongst the alloys dealt with are ferrosilicon and siliceous spiegel; and as these are of most common occurrence, those who may have them to examine often and have not simple methods of their own may be glad to know that the silicon may be determined with great rapidity and accuracy. It has been stated on many occasions, and it is a general impression, that high percentage ferrosilicon and siliceous spiegel are very imperfectly attacked by nitrohydrochloric acid, and that these alloys cannot be decomposed in this way.

This misconception has arisen from two causes; in the first place, if the alloy is not in a fine state of division the particles are coated with a layer of silica which prevents all further action of the acid. In the second place, where the alloy has been sufficiently pounded, after the usual treatment with the acid, the mixture is always evaporated to dryness and gently heated in order to render insoluble that silica which may have passed into solution. After then dissolving the residue in hydrochloric acid, filtering and washing, and igniting, the silica thus obtained is always contaminated largely with oxide of iron; this circumstance has naturally produced the impression that the alloy is only partially decomposed.

This, however, is not the case; if the ferrosilicon or siliceous spiegel be in a very fine state of division, vigorous boiling with nitrohydrochloric acid will perfectly decompose it in fifteen minutes. The silica which is formed is contaminated only with graphite. The physical condition of this silica, however, is so peculiar that if it be gently heated in contact with an iron salt in the dry state, it takes up ferric oxide and retains it with such tenacity that no ordinary amount of boiling with hydrochloric acid will purify it.

This peculiarity of course at once suggests that it is simply necessary to filter off the silica before evaporating, and evaporate the filtrate to dryness by itself in order to obtain the small quantity of dissolved silica.

In dealing with low percentage alloys, the quantity of silica which passes into solution is much greater than in the higher ones, and I have generally found the quantity to vary from 0·1—0·3 per cent in alloys containing from 10—15 per cent silicon. For works purposes, therefore, an addition of 0·2 per cent may be made to the quantity found by filtering off at once and the evaporation to dryness safely omitted. In this way the operator may have the silica ready to ignite in thirty minutes from the time of weighing out.

In conclusion, I would specially point out that the rapidity and perfectness of the decomposition in nitrohydrochloric acid depends entirely upon the fineness of the particles, and to secure this, after the usual treatment in the steel mortar and passing through the sieve, the small quantity necessary for the determination is ground as fine as possible in the agate mortar.

The method above described has been in use in the Newburn Steel Works' laboratory for nearly ten years, and it is rare that a silica is obtained which is not perfectly white after ignition over the blowpipe.

I need hardly allude to the fact that occasionally titanic acid may be present, and in cases where great accuracy is required this may be separated in the usual way by treatment with sulphuric and hydrofluoric acids.

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# ON THE CATALYTIC ACTION OF ALUMINIUM CHLORIDE ON SILICIC ETHERS.*

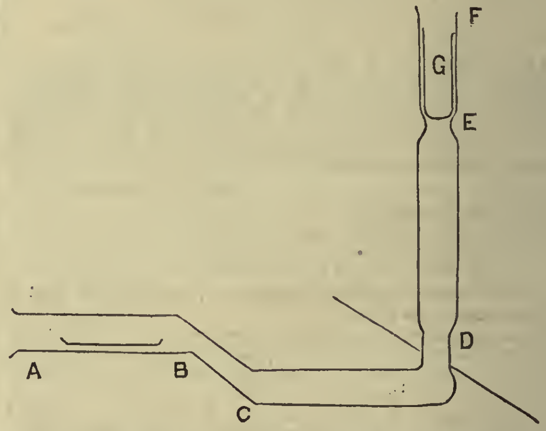
By H. N. STOKES.

(Concluded from p. 17).

### *Experimental Details.*

**Only** carefully fractioned silicates and freshly sublimed aluminium chloride were used. The apparatus and method of working were as follows:—

A thin-walled glass tube of about 2 c.m. diameter was drawn out into the shape shown in the figure. The constriction E served when necessary as a support for the small weighed test-tube G, in which the ethyl ether collected. Some aluminium chloride was placed in a boat, inserted into AB, and carefully sublimed over into CD in a current of dry hydrogen. In this way it was obtained in a finely divided state, rendering solution more rapid. The hydrogen was then replaced by air, BC drawn out and melted off at B, and the weight of the sublimed chloride determined to a centigram. CD was then placed in ice, the calculated weight of silicate or chlorsilicate introduced through F, the tube G inserted when necessary, and the apparatus attached to an inverted condenser which ended in a U-tube with two cocks, placed in a freezing mixture, and serving to condense the ethyl chloride and any ethyl ether that might be carried over. By gently agitating the tube, the solution of the chloride was effected. On removing from the ice, the reaction usually began of itself, and often had to be moderated by cooling. After the evolution of ethyl chloride had slackened, CD was gently heated, the ethyl ether then distilling and collecting in G. After the collection of ether had ceased, G was gently warmed, whereby practically all ethyl chloride was driven over, the ether condensing and running back. After removing G, the point B was broken off and the residue heated in a current of hydrogen until no further effect was observed, any aluminium chloride condensing in DE, or sometimes in part, being carried over into the condenser. The hydrogen was then displaced, DF melted off at D, when necessary, and all products determined by weighing. Some of the liquid in the U-tube was brought into a graduated tube over mercury, and any ethyl ether determined by absorption with a drop or two of strong sulphuric acid, the residue being ethyl chloride.



### *Ethyl Trichlorsilicate.*

Taken $SiCl_3(OR)$ 7·66 grms. (3 mol. wts.) and $AlCl_3$ 1·91 grms. (1 mol. wt.).

On removing the ice from CD, the evolution of ethyl chloride began almost at once, and the liquid grew so warm that cooling had to be resorted to to prevent the contents from boiling over. Presently a large quantity of a colourless, apparently crystalline substance separated, nearly filling the liquid. Its nature was not determined, but it was found to fuse on gently heating. After the evolution of ethyl chloride had moderated, its formation was promoted by a gentle heat. The liquid then became gradually thick, and finally almost solid. B was then broken off, and the residue heated in a stream of hydrogen until no further sublimation of aluminium chloride was observed. Absolutely no ethyl ether was formed. The residue was somewhat discoloured, solid, transparent, and frothy. As explained above, the reaction occurs in accordance with the equation—

$$SiCl_3(OR)+xAlCl_3=SiOCl_2+RCl+xAlCl_3,$$

as is borne out by the following data, which in this as in all following experiments are given in percentage of the total material used.

| | Found. | Calculated. |
|---|---|---|
| Residue . . . . . . | 46·3 | 51·2 |
| Sublimate ($AlCl_3$) . . | 20·9 | 19·9 |
| Distillate, RCl . . . . | 22·5 | 28·8 |

The results are naturally only approximate, but quite as near as could be expected. The viscosity of the liquid towards the end interferes with the smoothness of the

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* From the *American Chemical Journal*, vol. xiv., No. 6.

reaction, and it is impossible to condense the ethyl chloride completely, or to prevent some being carried off by the current of hydrogen. If the reactions given are correct, the residue is not really $SiO.Cl_2$, but a mixture of oxychlorides in which there remains a small amount of ethyl, which will not go off at a temperature below that at which carbonisation and other secondary changes take place, and which are still greater in the cases below mentioned. Troost and Hautefeuille (*loc. cit.*) have shown that the result of heating oxychlorides is an approximation towards $SiO_2$ and $SiCl_4$. This is doubtless the reason why in this case the weight of the residue is slightly too low, and that of the sublimed aluminium chloride a little too high. The former, on extracting with alcohol, left a little silica in gelatinous form, while the latter was found to contain a small amount of volatile silicon compounds. In fact, the residue, on heating in a test-tube to redness, gave off a considerable amount of volatile oxychlorides, but no aluminium chloride.

In experiment 2 the proportions taken were the same and the observations essentially similar.

| | Found. | Calculated. |
|---|---|---|
| Residue .. .. .. | 38·9 | 51·4 |
| $AlCl_3$ (sublimed) .. | 21·2 | 19·8 |
| RCl .. .. .. .. | 22·4 | 28·8 |

The residue consisted mostly of oxychlorides soluble in alcohol, and considerable silica insoluble in alcohol. A portion of the same residue gave—

| | Found. | Calc. for $SiO.Cl_2$. |
|---|---|---|
| Si .. .. .. | 27·08 | 24·35 |

The excess of silicon is due, as before, to a partial volatilisation of oxychlorides with a low percentage of silicon. This residue also contained a very small amount of aluminium, which was completely extracted by alcohol, and therefore present as chloride, not as silicate or oxide. No ethyl ether was formed.

In experiment 3, the residual aluminium was determined in the residue after heating to dull redness in hydrogen. The amount found, calculated as chloride, was only 3·5 per cent of the total chloride used. A small amount was to be expected, as it is practically impossible to expel it completely from the solid frothy residue. The conclusion that the chloride remains unchanged at the end of the reaction may therefore be accepted without hesitation.

### *Ethyl Dichlorsilicate.*

This calls for the reaction—

$$SiCl_2(OR)_2+xAlCl_3=SiO_2+2RCl+xAlCl_3.$$

Two experiments were made, one with Si : Al = 50 : 1, the second with Si : Al = 3 : 1. In both cases the decomposition was readily brought about; in the first almost as easily as in the second, but only in the second could any aluminium chloride be recovered, and then not the whole amount used. A small amount of ethyl ether was also formed in each case. As there were reasons for suspecting the sample to contain monochlorsilicate (which would explain the discrepancy), and as no more was available, the quantitative data are omitted.

### *Ethyl Monochlorsilicate.*

Four experiments were made, in which the following proportions were observed:—

$$Si : Al = \begin{cases} 3:3 & (1). \\ 3:2 & (2). \\ 3:1 & (3). \\ 150:1 & (4). \end{cases}$$

For case (1) the following equations hold, according as the chlorine of the aluminium chloride is completely given off as ethyl chloride, or as it remains in part as $\begin{matrix}O\\O\end{matrix}\!>\!AlCl$.

(*a*) $3SiCl(OR)_3+3AlCl_3=Si_3Al_2O_9+9RCl+AlCl_3.$

(*b*) $3SiCl(OR)_3+3AlCl_3=3(SiO_3AlCl)+9RCl.$

Taken, 6·21 grms. $SiCl(OR)_3$ and 4·19 grms. $AlCl_3$, or equal mol. wts.

The course of the reaction was essentially the same as with the trichlorsilicate, except that no solid was deposited. The liquid became gradually thicker, with evolution of ethyl chloride, and then quite suddenly stiff at about 75°. On heating in a current of hydrogen, a considerable volume of uncondensible hydrocarbon gas was given off, whereby some aluminium chloride was carried into the condenser and receiver. This was collected and determined. The amount of aluminium fixed in the residue was also determined. No ether collected, and none could be found by absorption over sulphuric acid.

| | Found. | Calculated for (*a*). | Calculated for (*b*). |
|---|---|---|---|
| Residue .. .. | 37·5 | 28·4 | 45·9 |
| Al in residue .. | 7·3 | 5·4 | 8·1 |
| $AlCl_3$ (sublimed) | 3·5 | 13·5 | — |
| $R_2O$ .. .. .. | — | — | — |

The reaction occurs, therefore, in a form combining (*a*) and (*b*), the residue probably consisting in part of aluminium silicates, in part of chloraluminium silicates.

For case (2), where Si : Al = 3 : 2, there are also two ultimate equations possible—

(*a*) $3SiCl(OR)_3+2AlCl_3=Si_3O_9Al_2+9RCl.$

(*b*) $3SiCl(OR)_3+2AlCl_3=Si_3O_8Al_2Cl_2+7RCl+R_2O.$

Taken, $SiCl(OR)_3$, 12·93 grms.; $AlCl_3$, 5·80 grms.; or exactly 3 : 2 mol. wts. The reaction was essentially similar to that in the last experiment, and took place quite as readily as when more chloride was used. The same gradual thickening and sudden stiffening of the liquid were noticed. On finally heating to dull redness in hydrogen, gas was evolved, and a somewhat carbonaceous black vitreous residue was left, but no aluminium chloride sublimed. A small amount of ethyl ether was formed, which was determined by absorption.

| | Found. | Calculated for (*a*). | Calculated for (*b*). |
|---|---|---|---|
| Residue .. .. | 36·0 | 32·7 | 39·1 |
| Al in residue .. | 6·1 | 6·2 | 6·2 |
| $AlCl_3$ (sublimed) | — | — | — |
| $R_2O$ .. .. .. | 2·5 | — | 8·6 |
| RCl .. .. .. | 33·5 | 67·3 | 52·3 |

Here, too, the reaction is intermediate between (*a*) and (*b*), some $R_2O$ is formed, but all aluminium remains in the residue.

Case (3), where Si : Al = 3 : 1, also admits of two equations—

(*a*) $6SiCl(OR)_3+2AlCl_3=Si_6Al_2O_{15}+12RCl+3R_2O.$

(*b*) $6SiCl(OR)_3+2AlCl_3=Si_6Al_2O_{14}Cl_2+10RCl+4R_2O.$

Taken, $SiCl(OR)_3$, 14·72 grms.; $AlCl_3$, 3·30 grms., or 3 : 1 mol. wt. The same thickening and sudden stiffening at 75° were observed. The reaction began at the same low temperature, and was nearly as rapid as with more chloride. Ethyl ether collected in the tube G in abundance, and was identified by its boiling at 30°—35°. The solid residue was nearly colourless, and only on high heating did discolouration ensue. No chloride sublimed. The ether was determined by weighing that collected, and absorbing the small amount found in the distillate as before.

| | Found. | Calculated for (*a*). | Calculated for (*b*). |
|---|---|---|---|
| Residue .. .. | 43·1 | 31·7 | 38·4 |
| $AlCl_3$ (sublimed) | — | — | — |
| $R_2O$ .. .. .. | 20·0 | 15·2 | 22·0 |

Although the residue was somewhat too large, the amount of ether showed that the reaction was mainly in the sense of (*b*).

Case (4). In this experiment 1 mol. wt. aluminium chloride was made to act on 150 mol. wts. monochlorsilicate, or almost a mere trace of the former (taken, 13·38 grms. silicate to 0·06 grm. chloride). The facts noted were the same as in the other experiments, including the sudden solidifying of the residue. The only difference was that the reaction took place rather more slowly, owing to the small amount of chloride present, and that the residue left at red heat was of purplish colour, showing very little carbonisation. The ease with which the decomposition took place indicated that a much smaller amount of aluminium chloride would have been sufficient. The ethyl ether showed the correct boiling-point.

The equation for a trace of aluminium chloride is practically—

$$SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

The actual results were :—

| | Found. | Calculated for Si : Al = 150 : 1. |
|---|---|---|
| Residue .. .. .. | 30·8 | 30·3 |
| $R_2O$ .. .. .. .. | 32·7 | 36·8 |
| RCl .. .. .. .. | 11·2 | 33·0 |

The amount of ether was 89 per cent of the theoretical.

### *Tetraethyl Silicate.*

Four experiments may be mentioned, into which the following proportions entered :—

$$Si : Al = \begin{cases} 3 : 4 & (1). \\ 3 : 1 & (2). \\ 3 : 0{\cdot}9 & (3). \\ 150 : 1 & (4). \end{cases}$$

The hypothetical equations for (1) and (2) are given under the general considerations on the decomposition of the tetraethyl silicate (*a*, *b*, and *c*).

For experiment (1) were taken 5·95 grms. $Si(OR)_4$, 5·09 grms. $AlCl_3$, or 3 : 4 mol. wts. It was not possible to cause the chloride to dissolve completely in this amount of ether, and the result was a mixture of varying composition, from which no definite result could be expected. The general course of the reaction was the same as in other cases. Some ethyl ether was formed, but a little aluminium chloride also sublimed, indicating an excess in one part of the mass and a deficiency in another.

In experiment (2) with Si : Al = 3 : 1 the mixture evolved ether and ethyl chloride, and finally became solid, and on further heating gave off gases, but no aluminium chloride. Only about one-half the theoretical amount of ether was obtained, the remainder appearing as hydrocarbon gas and empyreumatic substances.

In experiment (3) with Si : Al = 3 : 0·9 it was noticed that some unchanged silicate distilled at the end of the operation. It appears, therefore, that the least amount of aluminium chloride required to effect total decomposition is 1 mol. wt. to 3 mol. wts. of the silicate. This is strikingly seen in the next experiment (4), which at the same time shows the radical difference in their behaviour towards aluminium chloride of the silicates and chlorsilicates.

Taken, 16·37 grms. $Si(OR)_4$, 0·07 $AlCl_3$, or 150 : 1 mol. wts. Even on boiling strongly for an hour at about 165°, no marked reaction was noticed. The liquid remained clear and limpid, and not over 0·1 grm. ethyl ether collected. At the end of an hour the silicic ether was distilled off unchanged, leaving but a trace of solid residue. It was therefore clear that only a trace had been decomposed, corresponding to the trace of chloride used.

The decomposition of monochlorsilicates by a trace of aluminium chloride might perhaps be utilised to obtain other ethers than ethyl ether. It is known that the continuous process for obtaining ethyl ether from alcohol by means of sulphuric acid does not apply to the alcohols above propyl alcohol (Norton and Prescott, *Amer. Chem. Journal*, vi., 241). Isobutyl alcohol, for instance, does not give a trace of isobutyl ether. The silicates of the monatomic aliphatic alcohols, as far as has been investigated, are easily prepared, and of all the chlorsilicates the monochlorsilicates are the most easily made. By adding to 1 mol. wt. silicon tetrachloride 3 mol. wts. of the alcohol, boiling the product or heating to 170° under pressure, and finally distilling with a trace of aluminium chloride, a product should be obtained consisting of a mixture of ether and chloride which could be easily separated. From ethyl monochlorsilicate 89 per cent of the theoretical yield of ethyl ether was thus obtained.

### *On the Isolation of the Intermediate Products.*

Aluminium chloride is insoluble in carbon bisulphide if, however, a mixture of about 1 vol. tetraethyl silicate and 4 vols. carbon bisulphide be boiled with some aluminium chloride, the latter liquefies and partly dissolves, while there is an evolution of permanent gas, presumably ethyl chloride. On decanting the warm liquid a considerable amount of oil separates. This oil is not volatile, and on heating gives a solid residue resembling that obtained by the direct action of the chloride on the silicic ether. The carbon bisulphide solution, if concentrated out of contact with moisture, deposits on cooling a mass of well formed rectangular crystals, or on evaporation *in vacuo* over paraffin shavings leaves a perfectly dry crystalline mass. A portion of such a bisulphide solution was decomposed by ammonia, and the ratio of Si : Al : Cl determined. It was found to be 1 : 2·1 : 3·9, or very nearly 1 : 2 : 4, a result which may, of course, have been accidental. The oil which separates is soluble in a fresh portion of hot carbon bisulphide, but it appears readily to change, for a greater amount is required than that from which it separated, and by boiling out with small quantities of bisulphide, a residue is left which is finally almost solid. These facts seem to indicate the possibility of isolating some of the intermediate products, but this has not yet been attempted.

In conclusion, I wish to express my thanks to the Director of the Geological Survey, and to Prof. F. W. Clarke, for the means and opportunity of carrying out these experiments.

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## THE VOLUMETRIC ESTIMATION OF ZINC.

By BERTRAND C. HINMAN, Ph.B., A.M.

The Colorado Scientific Society outlined a plan, some time ago, of endeavouring to establish a uniformity in the technical methods of analysis in the West. For its first effort, a committee of several chemists was appointed to investigate the methods for the determination of zinc in ores, and their report was presented in June, 1892.

The ores submitted were from widely separated localities in Colorado; they were mixtures of galenite, pyrite, and sphalerite, accompanied by greater or less percentages of manganese in the form of rhodochrosite, associated with a quartzose gangue.

To obtain a standard of comparison, the samples of ore submitted by the committee were analysed by Mr. L. G. Eakins, of the U.S. Geological Survey. The method followed by him was the conventional one—in short, as follows:—

The ore was extracted with aqua regia, and the solution precipitated with sulphuretted hydrogen. In the filtrate from this precipitation, the iron was separated by precipitating twice as basic acetate, and once with ammonia. In these filtrates, combined and acidulated with acetic acid, the zinc was precipitated as sulphide, dissolved, precipitated as carbonate, and weighed as oxide.

Several chemists of metallurgical works in Colorado made analyses of the samples, and their methods and results are given in the report. They were, however, essentially like, or modifications of, the method of Messrs. Von Schulz and Low, which received the approval of the committee. (See *ante*, p. 6).

The ores upon which these experiments were made were all from one section of country, and, in general, were ores adapted to lead smelting. It seemed advisable, therefore, to try the method upon ores from other places containing associated minerals different from the above. The Franklinite and calamine ores are among the most important sources of zinc, and are very frequently dealt with in the metallurgy of that metal. Upon such ores most of the experiments were made.

The solutions were prepared as directed, with the exception that, for standardising, metallic zinc was used instead of the oxide. The standardising of the ferrocyanide solution presented no difficulty. If the solution is hot, the end-reaction shows promptly, but the amount of hydrochloric acid present must be regulated with some care, as an excess over that used at the time of standardising will delay the end-reaction in titration to a sensible degree. The practice adopted in making these experiments was to add a drop or two of methyl orange (though other indicators will answer equally well), bring the solution to the neutral point, and then add a known excess of hydrochloric acid. The colour produced by the indicator in no wise interferes with the end-reaction during titration. By observing this simple precaution, the solutions may always be of the same degree of acidity, insuring perfect uniformity in the appearance of the end-reaction.

At times, in dissolving the ore, all the potassium chlorate will not be decomposed, so that, when the solution is made acid with hydrochloric acid, just prior to titration, euchlorine will be set free. When using an indicator to determine the neutral point, its presence is manifested by its bleaching action upon the colour. It is well, then, to add a few drops of a solution of an alkaline sulphite.

To test the process, a calamine ore containing 66·80 per cent of zinc was carefully treated by the above-described method. There was obtained 65·14 per cent of zinc. The ore contained but little manganese, and the precipitate produced by the addition of the excess of ammonia consisted almost entirely of ferric hydrate. The residue and the precipitate was treated again with the chlorate mixture, the solution obtained evaporated to dryness, an excess of ammonia again added, and in the filtrate from this precipitation was found 1·62 per cent of zinc, making a total of 66·76 per cent. The experiment was repeated twice more in the same manner as at first. The three results were as follows:—

| | First Extraction. | Second Extraction. | Total. |
|---|---|---|---|
| Per cent of zinc .. .. | 65·14 | 1·62 | 66·76 |
| " " .. .. | 65·37 | 1·41 | 66·78 |
| " " .. .. | 65·35 | 1·41 | 66·76 |

The precipitated ferric hydrate held each time about 1½ per cent of zinc. This is a well-known phenomenon, but no mention of it seems to have been made by Messrs. Von Schulz and Low in their description. This is undoubtedly because the ores worked by them contained so little iron that no appreciable difference was made by its presence.

In a fourth experiment on this ore an attempt was made to avoid the re-precipitation of the ferric hydrate by evaporating the solution of the ore in the acid to dryness, and taking up with water instead of ammonia. Ferric nitrate seems to lose its nitric acid more readily than zinc nitrate, and by proceeding in this manner a filtered solution may be obtained containing only a small amount of iron. There was, however, enough present, so that it was necessary to remove it with an excess of ammonia. There was found as a result 66·45 per cent of zinc.

In order to determine the effect which the presence of manganese might have, a grm. of this ore was mixed with 0·200 grm. of pyrolusite, and treated precisely as at first. There was found 66·76 per cent of zinc, the manganese not changing the result. Thinking, perhaps, that the manganese dioxide would not be sufficiently decomposed in the strongly oxidising solution used in decomposing the ore, another experiment was made upon the same ore with the same amount of pyrolusite present, but the mixture was first treated with hydrochloric acid to carry the dioxide of manganese into solution; nitric acid was added to expel the hydrochloric acid, and then the mixture was treated with the chlorate solution, and the analysis finished in the same manner as the previous ones. There was found 66·808 per cent of zinc.

It may be safely concluded, then, that the presence of manganese does not interfere, and that it can be completely separated from zinc by oxidation to manganese dioxide in nitric acid solution.

A Franklinite ore containing 20·86 per cent of zinc and considerable manganese was next tried. The first treatment of this ore gave as its result only 15·60 per cent. The residue re-treated with acid as before yielded 1·01 per cent, and the residue from this again treated gave up 0·50 per cent, making a total of 17·11 per cent of zinc, or nearly 4 per cent low. The experiment was repeated upon another portion of the same sample. There was found only about 15 per cent of zinc. The residue was re-treated as before, and a little over 1 per cent was found. The residue from this treatment was dissolved in hydrochloric acid, the iron separated as basic acetate, the filtrate made acid with acetic acid, sulphuretted hydrogen gas passed into it, and an abundant precipitate of zinc sulphide was obtained.

Evidently the solvent action of the nitric acid containing the potassium chlorate was not sufficient to completely decompose the ore, so in the next experiment the following treatment was adopted:—

The ore was first digested with aqua regia; nitric acid was then added, and the mixture evaporated until all the hydrochloric acid had been expelled, the whole evaporated nearly to dryness, the regular amount of the nitric acid solution of the potassium chlorate was added, and the analysis finished as usual. As a result of this procedure, there was obtained 20·81 per cent of zinc.

A Franklinite, containing 23·53 per cent of zinc, analysed in duplicate in this manner, gave results respectively 23·54 per cent and 23·34 per cent of zinc. Still another sample of the same kind of ore having 31·42 per cent was found by the same treatment to contain 31·613 per cent.

Some of the ores tried, although very finely pulverised in an agate mortar, were yet not entirely soluble in aqua regia, and it was necessary to fuse the residue in order to effect complete solution.

Copper was found to be easily separated in the manner described by the originators of the method, and the lead introduced, and that which might otherwise be present, was found to have no injurious effect. In fact, at the end of a titration with the brown tint just faintly showing with the uranium acetate, a large excess of lead acetate was added without changing at all the end reaction.

The method of von Schulz and Low, as given by them, will answer for ores easily decomposed and containing little or no iron, but to adopt the method to all ores of zinc or compounds containing it, cadmium alone excepted (which, if present, must be removed with sulphuretted hydrogen) certain modifications are necessary. Guided by the preceding experiments, the following practice would seen most advisable.

Pure metallic zinc is more easily obtainable for standardisation than the pure oxide. In standardising and in actual analysis, that the right degree of acidity be uniformly maintained, the use of a colour-indicator in the solution is advised. It seems to be easier and simpler to work to the neutral point this way than to do it by means of test-papers, and the slight tint of colour necessary to show the change to the eye does not impair the end reaction with the ferrocyanide.

The ore, if at all refractory, should be very finely pulverised. A few moments spent in grinding will be more than compensated in the ease with which solution may be obtained.

Treat the finely divided ore with *aqua regia* until there is obtained complete decomposition, or until no further action is perceptible. If the ore has not been thoroughly decomposed, evaporate to dryness, dehydrate the silicic acid, take up with dilute hydrochloric acid, filter off the insoluble matter, and fuse it with carbonate and nitrate of soda in a platinum crucible. Dissolve the fusion in hydrochloric acid, and add the solution to the major portion. The dehydration of the silicic acid will consume some time, but if the ore is highly siliceous, the gain of time in filtering the sandy precipitate of silica as contrasted with filtering the gelatinous silicic acid will be more than repaid. All the zinc in the ore will now be in solution as chloride. Add nitric acid and boil until all the hydrochloric acid has been expelled; evaporate nearly to dryness, add the usual quantity of nitric acid saturated with potassium chlorate, and evaporate to dryness. Add the ammonium chloride and ammonia, dilute with water, heat to boiling, and filter, washing with a weak solution of ammonium chloride made alkaline with ammonia. Transfer the precipitate from the paper, by means of a spatula and wash bottle, to the vessel in which the ore was originally decomposed, evaporate off the water, and treat again with the chlorate mixture in the same manner as before, adding the solution obtained by treatment with ammonia to the original one. Acidify to the right degree with hydrochloric acid, heat nearly to boiling, and titrate with the standard ferrocyanide as described.

The details of the method as here worked out are more numerous than those given in the original article of von Schultz and Low, but it is apparent that to secure accuracy of results under varied conditions, they are necessary. It is still very much shorter than the conventional one, and carefully worked ought to give results nearly, if not quite, as accurate, and certainly the difficulties in manipulation are not so great.

In conclusion I desire to thank Professor Elwyn Waller far his valuable suggestions in the preparation of this paper.—*School of Mines Quarterly*, xiv., No. 1.

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# SOME REMARKS ON THE EXAMINATION OF THE RARE GADOLINITE EARTHS, AND IN PARTICULAR ON DETERMINING THE EQUIVALENTS OF THESE EARTHS BY CONVERTING THE OXIDE INTO THE SULPHATE.

By GERHARD KRÜSS.

Last year I made known contributions to the chemistry of erbium and didymium (*Liebig's Annalen*, 265, 1), in which there are described some new methods for working up the earths of gadolinite. This investigation has been continued, especially as regards the earths of erbia, and before reporting in the following pages of this journal (*Zeit. der Anorganischen Chemie*) on the nature of erbium, holmium, and terbium, I wish to communicate some general observations on the elaboration of the rare earths in question; as also new methods for their separation.

L. F. Nilson and the author (*Berichte Deutsch. Chem. Gesell.*, xx., 2134) examined, six years ago, the region of the rare earths yielding absorption-spectra by means of the qualitative spectrum analysis of a large number of earthy materials. Experiments in the same direction were made soon after by P. Kiesewetter and G. Krüss. From these observations it appeared that, *e.g.*, erbia and holmia are of a more complex character than it has been hitherto supposed.

Subsequently I pursued the examination of those earths, no longer exclusively by qualitative spectrum analysis, as hereby, at most, the behaviour of the earths could be ascertained in a certain relation to light. I did not carry out a plan which I had drawn out some years ago to institute a quantitative spectroscopic analysis of the solutions of the earthy salts. In this way merely some insight into the composition of mixed solutions of the earths could be expected without yielding better means for separating the mixtures. I wish to point out that the proof whether a rare earth is really homogeneous or not cannot in all cases be obtained spectroscopically as easily as it is sometimes assumed.

In all investigations—qualitative or quantitative—of the absorption spectra of the earthy salts, the colourless constituents, of course, escape direct observation. On the other hand, it must be considered that in examining the emission spectrum of a mixed earthy chloride, the lines of all the single constituents are not always visible. Mixtures containing even several per cents of ytterbia yielded in many cases no ytterbia lines in the very same experimental conditions in which pure compounds of ytterbium gave a visible spark spectrum. This fact has been previously observed by Nilson, Thalén, and others.*

Nevertheless, both absorption and emission spectroscopy are certainly frequently important auxiliaries in examining rare earths; but these methods if used alone do not suffice for the certain recognition—even qualitatively—of all the constituents of an earthy mixture. Here, as well as in deciding on the homogeneity of a fixed earth, we can never dispense with the methods for determining the equivalent. They are in the study of the earths a means equal in importance to spectrum analysis; without them there is at present no control of the value of one or other of the qualitative methods for the separation of the earths. The experiments which the author described a year ago, in *Liebig's Annalen*, 265, 1), have been conducted from this point of view.

Recently there has appeared (*Ber. Deutsch. Chem. Ges.*, xxv., 390, 569) an extensive investigation of P. Schottländer in which the spectroscopic method has been exclusively employed. The author's procedure of checking the results of qualitative spectral analysis by spectrophotometric measurements is, without doubt, of great theoretical interest, but the chemistry of the didymium oxides investigated does not seem especially advanced hereby to that extent that we have now with one or the other oxide of the didymium earths presented to us in a really pure state. Theoretically, Schottländer, by his spectrophotometric measurements, arrives at the conclusion that the rare earths producing absorption spectra have not in general so complicated a composition as Krüss and Nilson have previously inferred from the qualitative examination of those spectra. This seems to hold good, though in a quite different sense, from what P. Schottländer and the author also conjectured years ago. In the meantime, an examination of the nature of erbia and the kindred oxides has been carried on for several years, and I shall therefore return to that point by the present opportunity. I must here remark that after reading Schottländer's last treatise I regretted that he undertook the laborious quantitative spectroscopic examination of twenty-four didymia spectra, when he could ascertain from several preliminary experiments made with solutions of chrome-alum that his eye was but scantily prepared for the investigation. For this purpose a systematically conducted preliminary training of the eye is necessary, extending over several weeks.

### *On the Determination of the Equivalents of the Earths by Converting the Oxide into Sulphate.*

If we desire to decompose a mixture of earths by any mixture whatever, and to form an opinion on the value of

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* Thus, L. F. Nilson, in his treatise on scandium (*Ber. Deutsch. Chem. Gesell.*, xiii., 1442), describes an earth containing 1·3 per cent ytterbia and 98·7 scandia, and says:—"As Thaléo, notwithstanding this considerable proportion of ytterbia, could find no foreign matter on its spectroscopic examination, the balance seems to be a far more sensitive instrument than the best spectroscope for testing the purity of two substances of so different atomic weights as Se = 44 and Yb = 173."

the method and the manner in which it acts, the method must sometimes be applied repeatedly, prolonged operations have to be carried out until distinct differences perceptible spectroscopically are obtained, and a certain decision may be reached.

In many cases differences in the composition of mixed earths may be found more rapidly, and in any case more certainly, by a determination of the equivalents of the earths.

This method has been already employed by several investigators. I need merely remind the reader of the isolation of scandia by L. F. Nilson. Generally speaking, however, this method is not preferred. The reason is probably that such careful gravimetric operations as the determinations of the combining weights of the rare earths are troublesome and tedious, especially when it is necessary for the object in view to effect hundreds of such analyses. Objections of another kind have also been advanced: calling in question the trustworthiness of the methods employed for determination and in part with right. The rare earths are generally not remarkably powerful bases; indeed, for the most part, they are feeble bases, so that the formation of basic salts may easily take place unless the earths are combined with decidedly strong acids. Hence the equivalents of the rare earths which have been deduced from the analysis of the chlorides, nitrates, and oxalates,* are possibly in many cases too high. The earthy sulphates should naturally yield the most trustworthy results, and their analysis has therefore been most frequently used for determining the equivalents of the earths.

On account of the tendency of barium sulphate to occlude other substances, it cannot be recommended to refer the equivalent of an earth to $BaSO_4$, as it has often been done.

This reference requires a greater number of operations, and consequently includes more sources of error than if a weighed sulphate is converted into an oxide of ignition, or an oxide is transformed into a neutral sulphate.

As in the four last years very many determinations of the equivalents of the earths have been carried out in my laboratory, it seems to me that the conversion of oxide into sulphate is generally preferable to the inverse process. This method yields more certain results, and at the same time, in the execution of many determinations, it admits of the simultaneous performance of a great number of experiments.

According to the literature to which I have access, this method was first applied by J. Bahr and R. Bunsen (*Zeit. Annalen*, 137, 21, 1866) in the examination of yttria. In like manner the conversion of oxide into sulphate was utilised by J. T. Cleve (*Bulletin Soc. Chimique* [2], 21, 196, and 246, 1874) in determining the equivalents of lanthana and didymia, as also in the determination of ytterbia and scandia by L. F. Nilson (*Ofvers ak Forh.*, 1880, No. 6, and *Ber. Deutsch. Chem. Gesel.*, xii., 550, and xiii., 1439). Although the names of these authors are a guarantee that this method is practicable, we find in those communications as to the manner of working by this method not more thorough-going instructions than the following:—That the oxide, chloride, or nitrate for conversion into sulphate is to be heated off with an excess of sulphuric acid at a temperature sufficient to expel free sulphuric acid, but not to form basic sulphate. Under certain circumstances this may be difficult, and in fact the earthy sulphates may be re-converted into earths by heating. I may further show that as G. H. Bailey (*Chem. Soc. Trans.*, 1887, 676—683) has pointed out some time ago, it is not possible to bring a didymium sulphate which contains excessive sulphuric acid to a constant weight by heating to 360°; on every further gradual rise of temperature a loss of weight occurs again, and at no degree of temperature can didymium sulphate, contaminated with an excess of acid, be brought to a constant weight. If Bailey's observations are correct, and if we consider that didymia is more strongly basic than scandia, ytterbia, or yttria, the conversion of these earths into sulphates, as undertaken by Bahr, Bunsen, and Nilson, can scarcely have been accurately practicable.

The author's own research was concerned with more feebly basic earths, the erbia-earths, the sulphates of which must certainly be still less stable than didymium sulphate. On this account I submitted the method of the determination of equivalents, the conversion of earths into sulphates, to the closest possible examination, especially as regards the stability of the earthy sulphates at the temperature at which the excessive sulphuric acid is expelled.

The earth, the equivalent of which is to be ascertained, was in the examples given below, and in all determinations of equivalents communicated by the author and his coadjutors in this and the following numbers of this journal, always again purified before its conversion into sulphate in the manner following:—Any traces of copper or platinum which might have been introduced in the course of the work were removed by passing sulphuretted hydrogen into the slightly acid solution of the earth; the earthy hydroxides were removed from the filtrate by means of ammonia, and washed for a long time to remove lime and magnesia. After dissolving in a little nitric acid and prolonged heating, the earths were precipitated as oxalates, filtered in a crystalline condition, and converted into earths by ignition in a porcelain crucible on the blast until the weight became perfectly constant.

If water or dilute hydrochloric acid is added to the oxides, a slight loss is easily occasioned by the formation of dust, wherefore the crucible containing the earth, protected by a dust-funnel, is placed first on a heated water-bath until the oxides have been slacked by the gradual access of watery vapour; solution is then effected by the addition of dilute hydrochloric acid and continued heating. After complete solution has been obtained, dilute sulphuric acid was added in moderate excess and concentrated as far as possible upon the water-bath. The sulphate then separates out in crystals. The elimination of the excessive sulphuric acid was effected first on an iron plate 2 decimetres square and 5 m.m. in thickness. To prevent spirting it was heated at first with a small flame, the point of which was at the distance of 4 c.m. from the plate. In this manner the concentration and evaporation of the excessive acid could be almost left to itself. The temperature was gradually raised, and after three hours the plate could be heated as strongly as it was possible by means of a powerful Bunsen flame placed immediately underneath.

After the visible evaporation in this manner has ceased, after about two hours it was heated with a triple burner, whereby the plate, if it rested upon an iron stand, never became red-hot under the crucibles.* The sulphate not yet perfectly driven off must not be left uncovered over night, as it would take up moisture and effloresce to loose masses like cauliflowers, and on further treatment it could scarcely be brought to a constant weight on account o its excessively large surface.

(To be continued).

Determination of Kreatinine in Urine.—Gautrelot and Vieillard (*Soc. de Medecine Pratique*).—The authors make three separate determinations of nitrogen, one in the original urine, a second in the same after precipitation with basic lead acetate, and a third after precipitation with basic lead acetate and zinc chloride.

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* The use of the oxalates for determining the equivalents of the earths will be considered in a subsequent memoir.

* The "fuming off" of the excessive sulphuric acid up to this point can, of course, be effected much more rapidly. This requires, however, continuous careful observation of the contents of the crucible, whilst if the above conditions are observed, the excessive sulphuric acid of many analyses can be simultaneously driven off without particular trouble.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, December 15th, 1892.*

Dr. W. J. Russell, F.R.S., Vice President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Pedrozo d'Albuquerque, Barbadoes, W.I.; William James Cowan, 77, Trinity Road, Wood Green, London; George Davey, Las Trojes Angangues, Michoacan, Mexico; Daniel O. Sydney Davis, Rhydfallen, Stonebridge Park, Willesden, N.W.; Samuel Felix Dufton, D.Sc., Spring Wood House, New Cross Street, Bradford; John Henry Evans, 71, Lamhton Road, Cottenham Park, Wimbledon; Charles Thomas Tyrer, Stirling Chemical Works, Stratford, E.; James Robert Thackrah, M.A., Technical Schools, Plymouth; John Cundell Wood, 3, Bedford Terrace, Sunderland.

The following were duly elected Fellows of the Society:—David Avery; Samuel Robert Adcock; William Smellie Anderson; Horace Vincent Butterfield; Arthur John Bensusan; Arthur James Cooper; Frederick Walter Carlton; Earnest Victor Clark; Andrew Campbell; Andrew William Craig; Lionel Cooper; Joseph R. Dennison; Thomas Duxbury; Martin Onslow Forster; William French; Walter Goodall; William Thomas Gronow; Thomas Gray; James G. Hardy; Walter S. Haines; Samuel C. Hooker, Ph.D.; Edgar Edward C. Horwill; John Horsfall, Walter Holinshed Ince, Ph.D.; John F. V. Isaac; Samuel Jackson; John Jackson; William George Johnston; G. Krause, Ph.D.; Kunwar Kishor Kacker; Thomas Torrens Knowles; Charles Thornton Lamb; Francis Colin Moorwood; John Bate Nicholls; James Wyllie Rodger; Hugh Ramage; Norman Scott Rudolf; James Robson; Augustus Schloesser, Ph.D.; Ernst Speidel, B.S.; George Arthur Shaw; Reginald des Forges Shepherd; William James Sell; Satvaprasad Sarbadhicary; Charles Spackman; Albert Henry Turton; N. T. M. Wilsmore; William Williams; Jno. Lowe Whiteside; Jno. Williams; Frederick Henry Wigham, Frederick William Westaway.

Of the following papers, those marked * were read:—

*82. "*The Identity of Caffeine and Theine and the Interactions of Caffeine and Auric Chloride.*" By Wyndham R. Dunstan and W. F. J. Shepheard.

Mays (*Journ. Physiol.*, vii., 458; *Therapeutic Gazette*, 1866, 587) and more recently Lauder Brunton and Cash (*Roy. Soc. Proc.*, xlii., 238; *Journ. Physiol.*, ix., 112) having concluded that "theine" from tea differs in its physiological action in certain respects from "caffeine" from coffee, the authors have deemed it desirable to compare the products from the two sources: they conclude that their identity is beyond question. The observed differences in physiological action must be ascribed either to impurities in the materials used, or to differences in the animals to which they were administered; the circumstance that "theine" has been found to be more active and to be capable of producing effects not produced by "caffeine" tends to support the view that the "theine" was impure, especially as it is known that tea contains other alkaloids.

It is found that when an aqueous solution of caffeine aurichloride is heated, a yellow flocculent precipitate of *aurochlorocaffeine* is gradually formed, the—

$$C_8H_{10}N_4O_2{\cdot}HAuCl_4$$

being resolved into $2HCl$ and $C_8H_9(AuCl_2)N_4O_2$; this substance is insoluble in alcohol, chloroform, and ether, but dissolves in chlorhydric acid, being re-converted into the aurichloride; it is contended that the production of this compound is better shown by Medicus's formula of caffeine than by that proposed by Emil Fischer. A compound of caffeine and potassium aurichloride is described, crystallising in dark red needles; it readily dissolves in alcohol and water, but apparently dissociates.

Discussion.

Professor Tilden, referring to his work on periodides of alkaloids published over twenty-five years ago (*C. S. Journ.*, xviii., 99; xix., 145), said that he had not been able to notice any difference between the periodides prepared from caffeine and theine.

*83. "*Studies on Isomeric Change.* (II.) *Orthoxylenesulphonic Acids.*" By Gerald T. Moody, D.Sc.

The results described in this and the following note have been obtained in the course of an investigation on isomeric change now being carried on at the Central Institution (*cf. Proc. Chem. Soc.*, 1888, 77); the object in view was to determine whether 1 : 2 : 3-orthoxylenesulphonic acid is converted on heating into 1 : 2 : 4-orthoxylenesulphonic acid. In order to prepare the 1 : 2 : 3-acid, orthoxylene was first treated with two molecular proportions of bromine, whereby it was converted into a mixture of the liquid and solid dibromo-orthoxylenes; the latter (m.p. 88°) — which has been shown by Jacobsen to have the constitution—

$$2CH_3 : 2Br = 1 : 2 : 4 : 5$$

—was sulphonated by very cautiously heating it in a water-bath with about ten times its weight of 15 per cent anhydrosulphuric acid until the mixture became liquid, then keeping it at 75°, with constant shaking, until complete dissolution of the oil was effected; the liquid solidified on cooling. The resulting sulphonic acid was converted first into barium salt and eventually into sodium salt. *Sodium dibromorthoxylenesulphonate*, $C_6HBr_2(CH_3)_2SO_3Na+1\frac{1}{2}H_2O$, crystallises in small scales, and is easily reduced on boiling it with zinc dust and sodium hydroxide, forming 1 : 2 : 3-sodium orthoxylenesulphonate. The latter crystallises in beautiful long flat monohydrated plates; unlike the sodium salt of the 1 : 2 : 4-acid, it does not effloresce in air. 1 : 2 : 3-orthoxylenesulphonic chloride crystallises from light petroleum in prisms melting at 47°, the sulphoamide crystallising from water in groups of needles melting at 167°.

The 1 : 2 : 3-sulphonic chloride was converted into the acid by heating 5 grms. of it with 20 c.c. of water in a sealed tube immersed in the vapour from boiling xylene, the tube being, from time to time, removed from the bath and shaken; the resulting solution was cautiously evaporated on a steam-bath. The crystalline acid thus formed remained dry on being exposed to the air for several days; a small portion was converted into sulphonamide, which melted sharply at 167°, showing it to be the unchanged 1 : 2 : 3-acid; the rest was placed in a tube standing in an oil-bath heated at 115—120°, and a current of dry air drawn over it during two hours, at the end of which time the acid has become dark grey in colour. The sulphonamide prepared from the thus-heated acid melted sharply at 144°, showing that the 1 : 2 : 3-acid had been completely converted into the isomeric 1 : 2 : 4-acid. On repeating the experiment, the same result was obtained; and it is worthy of remark that in both cases only a very slight indication of the formation of sulphuric acid was obtained.

*84. "*Studies on Isomeric Change.* (III.) *Phenetoilsulphonic Acids*, $C_6H_4(OEt)SO_3H$." By Gerald T. Moody, D.Sc.

In a note published early in the year (*Proc. Chem. Soc.*, 1892, 90) the author stated that only one sulphonic acid is formed by the interaction of sulphuric acid and phenetoil under ordinary conditions; Lagai not long afterwards controverted this statement (*Ber.*, 1892, 1839) and asserted that he had isolated a second acid from the product of sulphonation; describing its chloride as a syrupy liquid, and its amide as crystallising from water in feathery needles melting at 142°. Lagai, however, quoted no analyses, or other evidence to show that his compound melting at 142° was really a derivative of phenetoil.

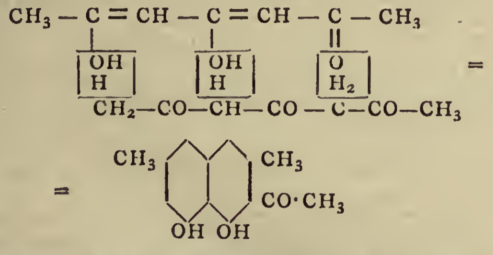
In order to obtain the orthophenetoilsulphonic acid, parabromophenol was ethylated. The bromophenetoil thus formed boiled constantly at 228—230°, and readily sulphonated when shaken with an equal bulk of ordinary oil of vitriol. The resulting bromophenetoilsulphonic acid crystallised from the acid solution in characteristic prisms. It was readily reduced by digestion with zinc-dust and sodium hydroxide solution. The sodium salt of the resulting ortho-acid, $C_6H_4(OEt)SO_3Na+H_2O$, crystallised in slender needles; it afforded a sulphonic chloride which crystallised from light petroleum in thin plates melting at 62°, from which a sulphonamide was obtained, crystallising in very long flexible needles, melting at 156°. These melting points place beyond doubt the fact that Lagai's compound melting at 142° is not phenetoilorthosulphonamide. On the other hand, the sulphonic acid giving a chloride and amide melting at 62° and 156°, respectively, is shown to be a phenetoil derivative by its behaviour on heating. The pure acid was formed by digesting the sulphonic chloride melting at 62° with dilute alcohol for twelve hours, and then evaporating the solution; it was obtained as a crystalline mass, permanent in air. A small quantity of this product was converted into sulphonamide, which was found to melt at 156°; the remainder was placed in a tube contained in an oil bath and heated for three hours at 100°, a current of dry air being passed through the tube; during the process, the acid darkened somewhat in colour, and was eventually found to contain a minute quantity of sulphuric acid. The acid thus heated gave a sulphonamide which melted sharply at 150°, showing that a complete change to the para-acid had taken place.

*85. "*Formation and Nitration of Phenyldiazoimide.*" By WILLIAM A. TILDEN and J. H. MILLAR.

Phenyldiazoimide, $N_3\cdot C_6H_5$, is readily prepared by the interaction of nitrosyl chloride and phenylhydrazin dissolved in excess of glacial acetic acid, together with only a small quantity of resinous by-products. When gently heated with ordinary strong nitric acid, the imide yields about two-thirds of its weight of the paranitro-derivative (m. p. 74°), together with smaller quantities of two crystalline by-products not yet fully examined. Nitrophenyl diazoimid forms a convenient source from which to obtain Curtius's diazoimide, about 40 per cent of the calculated quantity of the compound being obtained, as shown by Noelting, Grandmougin, and Michel (*Ber.*, xxv., 3328), on boiling it with alcoholic potash.

*86. "*The Production of Naphthalene Derivatives from Dehydracetic Acid.*" By J. N. COLLIE.

The author has further examined the yellow substance referred to in his previous notice (*Proc. Chem. Soc.*, 1892, 188), and arrives at the conclusion that the condensation of diacetylacetone probably occurs in the following manner:—



At first he was inclined to the belief that the substance was a quinone, but, as all attempts to reduce it failed, and as it did not, in other respects, behave as a quinone, he has abandoned the idea; moreover, it is impossible to explain the formation of a quinone from diacetylacetone by any simple interaction such as the mere elimination o the elements of water involves.

The substance yields a diacetyl derivative when heated with acetic anhydride, and affords bromine substitution derivatives when treated with bromine. A trimethylnaphthalene is produced on distilling the diacetate with zinc dust.

Finally, it is pointed out that the 2-aceto-1-naphthol described by Wilt (*Ber.*, xxi., 321) and the 3-aceto 1-naphthol prepared by Erdmann (*Ibid.*, p. 635) closely resemble the compound from diacetylacetone.

87. "*A New Synthesis of Hydrindone.*" By F. STANLEY KIPPING, Ph.D., D.Sc.

In a previous note (*Proc. Chem. Soc.*, 112, 107) it has been stated that a hydrocarbon of the composition $C_3H_2$ and other compounds are produced by the action of phosphoric anhydride on phenylpropionic acid; as the whole behaviour of the hydrocarbon pointed to its having a high molecular weight, it seemed probable that its formation was brought about by the condensation of two or more molecules of some intermediate product, possibly hydrindone. As this assumption could only be satisfactorily settled by preparing the hydrocarbon from hydrindone, attempts were made to synthesise the latter by treating phenylpropionic chloride with aluminium chloride; a few trials had already been made, with but slight success, when the writer's attention was called to a note by Hughes (*Proc. Chem. Soc.*, 96, 70), in which similar experiments with phenylpropionic chloride, carried out at Marsh's suggestion, were described; on continuing the experiments, it was soon found that, although Hughes failed to obtain hydrindone, it can be easily prepared in large quantities by the method suggested, and that, under suitable conditions, the yield of pure compound is 50—60 per cent of the theoretical, its formation being expressed by the equation—

$$C_6H_5\cdot CH_2\cdot CH_2\cdot COCl = C_6H_5{<}\begin{smallmatrix}CH_2\\ CO\end{smallmatrix}{>}CH_2 + HCl.$$

The ketone prepared in this way crystallises in colourless waxy plates melting at 41—42°, and is identical with the hydrindone obtained by Gabriel and Hausmann (*Ber.*, xxii., 2019) from ethylic orthocyanobenzylacetate, and by König ("Inaug. Diss." Leipzig, 1889) from orthocarboxyhydrocinnamic acic.

Several derivatives of hydrindone have been prepared and characterised:—The hydrazone, $C_{15}H_{14}N_2$, crystallises from dilute alcohol in almost colourless needles melting at 127—128°. The *hydroxime*, $C_9H_8{:}NOH$, crystallises from benzene in colourless needles melting at 140—141°. The *nitro*-derivative, $C_9H_7O\cdot NO_2$, is a colourless crystalline substance melting at 75—76°.

When heated with moderately concentrated sulphuric acid, hydrindone yields a compound of the composition $C_{18}H_{14}O$; this condensation product crystallises from dilute alcohol in yellowish plates melting at 141·5—142·5°. When warmed with phosphoric anhydride, hydrindone is converted into a yellowish crystalline substance, which, judging from its general behaviour, is identical with the hydrocarbon obtained by treating phenylpropionic acid with phosphoric anhydride.

The investigation is being continued in other directions, as it appears probable that similar intramolecular condensations may be brought about in the case of other benzenoid compounds containing a side chain with the aid of aluminium chloride.

88. "*The Re-solution of Methoxysuccinic Acid into Its Optically Active Components.*" By T. PURDIE, Ph.D., B.Sc., and W. MARSHALL, B.Sc.

The authors find that inactive methoxysuccinic acid—prepared from fumaric acid by the addition of the elements of methylic alcohol—can be resolved into optically active components by means of the acid cinchonine salt, the salt of the dextrogyrate acid being less soluble in water and crystallising more readily than the corresponding salt of the lævogyrate acid. The separation of the active acids effected in this manner, however, was only partial, the metallic salts obtained after removal of the cinchonine being mixtures of active with more or less inactive salt, from which the latter had to be separated by fractional precipitation or crystallisation.

In the first series of experiments the elimination of the inactive salt was effected by means of the different solubilities of the calcium and hydrogen potassium salts, the salts of the active acids being more soluble than those of the inactive acid. When solutions containing equal quantities of the oppositely active hydrogen potassium salts were mixed, the inactive salt was instantaneously precipitated.

The specific rotatory power of the active acids in a 5 to 10 per cent aqueous solution is about 33°; they melt at 88°—90°, the inactive acid melting at 108°. The specific rotatory power of the normal ammonium and potassium salts is of the same sign as that of the acids, but not so great, and it does not vary much with change of concentration; that of the calcium and barium salts is of opposite sign to that of the acid, and diminishes rapidly with decreasing concentration, the sign of the rotation of the latter salt being reversed in very dilute solutions.

89. "*Optically Active Ethoxysuccinic Acid.*" By T. Purdie, Ph.D., B.Sc., and I. Wallace Walker, M.A.

When spores of *Penicillium glaucum* are sown in a solution of the inactive acid ammonium salt of the inactive ethoxysuccinic acid formed by the addition of the elements of ethylic alcohol to fumaric acid, to which nutritive mineral salts have been added, an abundant growth of mycelium ensues, the result being that the lævogyrate component of the inactive acid is consumed, the dextrogyrate being left unaltered. The specific rotatory power of the acid in a 5 to 10 per cent solution is about +33°; it melts at 76°—80°, while the inactive acid melts at 86°.

The active acid ammonium salt crystallises with one molecular proportion, the corresponding inactive salt with half a molecular proportion, of water.

The inactive acid can also be resolved into its active components by means of the cinchonidine salt, the salt of the dextrethoxysuccinic acid being less soluble in water than its oppositely active isomeride. The active components were not obtained in the pure state by this process, but oppositely active acid ammonium salts were obtained which crystallise exactly like the salt produced by means of *Penicillium*, and whose specific rotations approximated in amount to that of the latter.

The authors find a close parallelism in respect of optical activity between the dextromethoxysuccinates, and dextrethoxysuccinates, the remarks about the former in the preceding abstract applying in general to the latter. The ethoxysuccinates are, however, more dextrorotatory or less lævorotatory than the corresponding methoxysuccinates.

The bearing of some of these observations on the theories advanced by P. A. Guye (*Annalen* [6], xxv., 145) and by Crum Brown (*Proc. R. S. E.*, xvii., 181) regarding the relations of optical activity to the nature of the radicles which are united to the asymmetric carbon atom is discussed.

90. "*The Formation of Benzyldihydroxypyridine from Benzylglutaconic Acid.*" By S. Ruhemann, Ph.D., M.A.

Ethylic benzylglutaconate (*cf. Annalen*, ccxii., 261) slowly dissolves in a concentrated aqueous solution of ammonia at 100°, forming a coloured liquid, from which acids precipitate benzyldihydroxypyridine,—a substance which exhibits both acid and basic properties. It crystallises in glittering plates which melt at 184°; its dibenzoate melts at 164°. On oxidation, it readily yields coloured products possessed of tinctorial powers.

91. "*The Action of Nitrous Acid on 1-α-amido-2-β-naphthol: a Correction.*" By R. Meldola, F.R.S.

In a paper published conjointly with G. T. Morgan (*Chem. Soc. Trans.*, lv., 114), wherein we had occasion to identify α-amido-β-naphthol in the presence of other bases, we stated that the yellow crystalline substance obtained by the action of nitrous acid was nitroso-β-naphthol. At the beginning of the present year a paper by Grandmougin and Michel appeared (*Ber.*, xxv., 972), in which these authors stated that the compound in question was β-naphthaquinone. I repeated the experiment at the time, and confirmed their statement. They have called attention to the discrepancy in another paper just to hand (*Ber.*, xxv., 3429), and ask for further details. In reply, I have only to state that I was not particularly concerned at the time with the nature of the crystalline compound, and it was not very closely investigated, as will be seen on reference to our paper (*loc. cit.*, p. 120). The superficial examination of the substance which we made led us to the belief that it was nitroso-β-naphthol, as it had a similar melting-point, and was soluble in alkali, and the subject was not further pursued, as it was beyond the scope of our investigation. The subsequent investigations by Grandmougin and Michel have convinced me that the substance which we had in hand was impure β-naphthaquinone, possibly mixed with some β naphthaquinoneanilide, owing to the retention of a trace of aniline salt. The formation of β-naphthaquinone by the action of nitrous acid on α-amido-β-naphthol is a most unexpected discovery, which could not possibly have been foreseen, and the credit of which is entirely due to these authors. I have frequently had occasion to repeat this test in the course of some recent investigations, of which the results will be communicated to the Society subsequently: the method described by Grandmougin and Michel is certainly the simplest and by far the most effective yet made known for preparing pure β-naphthaquinone in large quantities.

92. "*Note on the Action of Phenylhydrazine on Mono- and Di-carboxylic Acids at Elevated Temperatures.*" By W. R. Hodgkinson and A. H. Coote.

Phenylacetic acid and phenylhydrazine readily interact when heated together at 120°, forming—

$$C_6H_5{\cdot}N_2H_2{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5$$

(Bülow, *Annalen*, ccxxxvi., 196). In preparing this and similar hydrazides for another investigation, it was observed that a certain amount of decomposition took place, ammonia being one of the products. The course of the decomposition in the case of several monobasic benzenoid acids was, therefore, studied.

When heated with an equivalent quantity of phenylhydrazine, phenylacetic acid at first gives off water at temperatures up to 150°, the action then becomes more energetic, nitrogen and ammonia being evolved, light oils distilling over; and as the temperature is raised between 280° and 350°, a thicker oil distils over, a slight tarry residue being left in the retort. The lighter oils were found to consist of benzene and aniline. The greater portion of the heavy oil boiled between 320° and 370° C. On fractionating, a heavy substance was obtained boiling at about 340° free from nitrogen, which on analysis gave figures corresponding to the formula—

$$C_{14}H_{12}O_2 = C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5,$$

viz., 85·8 per cent carbon and 6·22 per cent hydrogen, the theoretical values being 86·0 and 6·12.

The decomposition cannot be very directly formulated. The first stage is the formation of the hydrazide—

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5;$$

but on heating this, NH·NH is split off, which immediately breaks up and reduces neighbouring molecules of phenylhydrazine partly to aniline and partly to benzene, with liberation of nitrogen and ammonia.

In the case of orthotoluic acid, $C_6H_4.CH_3.COOH$, a similar action takes place, but the amount of high boiling oil (ketone) is somewhat less, and the amounts of benzene and aniline somewhat greater.

In the case of phenylpropionic acid action also takes place in a manner analogous to that observed in the case of phenylacetic acid.

Some dibasic acids, for example, succinic acid, exhibit a behaviour similar to that described when heated with phenylhydrazine, ammonia and nitrogen escaping, while a high boiling oil, free from nitrogen, distils over.

The authors desire to reserve the further study of these interactions for a short time.

### *Kopp Memorial Lecture.*

An extra meeting of the Society will be held on February 20, 1893, at 8 p.m., the anniversary of the death of Hermann Kopp, when a lecture will be delivered by Professor Thorpe, F.R.S.

## CORRESPONDENCE.

### THE POSITION OF CHEMISTS.

*To the Editor of the Chemical News.*

Sir,—When Mr. Wm. Thomson states that a constant majority of the Council of the Institute of Chemistry has consisted of Fellows more interested in teaching than in the practice of consulting and analytical chemistry, it appears to me that he states what is not a fact, and publishes as widely as he possibly can that which is very misleading. I would, therefore, beg all those who have received his circulars to examine the *List of Officers and Council* printed in the Register for 1892 and judge for themselves.

Of those who are professors, lecturers, or teachers, I can count but eight out of a total number of twenty-seven ordinary members of Council. Even if we take into account the president, vice-presidents, and treasurer, only twelve out of the thirty-five individuals can be supposed to belong to the class to which Mr. Thomson refers.

"It seems curious, therefore, that the Council of the Institute should be composed chiefly of those who do not belong to the class of members (by far the largest) for whose benefit the Institute was specially founded." (See Mr. Thomson's letter, Chemical News, vol. lxvii., p. 23.)

If it were so it would be *very curious!*—I am, &c.,

W. N. Hartley.

January 14, 1892.

### POISONING BY $AsH_3$.

*To the Editor of the Chemical News.*

Sir,—As the cases of poisoning by this gas are rare, I beg leave to draw your attention to the first which has occurred in this country. The victim was the Professor of Chemistry and Mineralogy in the University of Chile (Santiago)—Dr. Hans Oscar Schulze—who for the last ten years had been engaged in the study of the conditions under which bodies take the colloidal state, having already succeeded in obtaining in this form the trisulphide of antimony.

On the 18th November (1892), he was occupied in the laboratory of the University in making a current of $AsH_3$ pass through a solution of $As_2O_3$, with the purpose of obtaining arsenic in a soluble form. It seems that the gas-generating apparatus was not hermetically closed, and let escape hydric arsenide in so small a quantity that its odour was not noticed by Prof. Schulze. One hour and a half after having commenced the operation this gentleman felt sick, and realised that he was poisoned by the $AsH_3$. He left the laboratory, but before doing so wrote in chalk by the side of the apparatus, "Cuidado, $AsH_3$!" (take care!).

Five days afterwards he was dead,—all efforts having proved useless to counteract the action of the poison. Nothing could arrest the progress of the uræmia and the rapid destruction of the red corpuscles (the number of which decreased to 1,800,000 per cubic millimetre), and the fatty degeneration of the tissues.

Prof. Schulze had studied in Freiberg and in Leipzig; his numerous and important papers on chemistry and mineralogy have been published in the scientific periodicals of his country, Germany.—I am, &c.,

Q. Newman.

Valparaiso, Laboratory of Chemistry,
Naval School, December 8, 1892.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 1, January 2, 1893.

This number contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. vii. and viii., No. 24.

**Determination of the Acidity due to the Fixed and the Volatile Acids of Wine.**—J. A. Müller.—The determinations of potassium bitartrate of tartaric acid, succinic acid, and tannin being effected, the acidity of the fixed acids enables us to find the quantity of the other acids such as the malic, or of acid salts which may be present. On the other hand, the standard of the volatile acids shows whether the wine examined is sound or diseased. He takes first the total acidity in 10 c.c. by means of a standard baryta-water, 1 c.c. of which corresponds to 0·01 grm. of sulphuric acid, using as indicator an alcoholic solution of phenolphthaleine at 5 grms. per litre; 10 c.c. of the wine are then put in a flask containing about 100 c.c., the neck of which is connected to a water-sprengel. A vacuum is made and maintained for ten minutes, agitating briskly towards the end to facilitate the expulsion of the last fractions of the dissolved gases. The total acidity is again determined. To find the acidity due to the fixed acids and to their acid salts, M. Müller evaporates 10 c.c. of the wine in a porcelain capsule of 12 c.m. in diameter and having a round bottom. The evaporation is made over a small Bunsen flame, holding the capsule by the spout. A rotatory movement is given to the liquid, and the surface is blown upon from time to time to eliminate the vapours. The evaporation lasts only a few minutes, and the residue is dried for two to three minutes, taking care not to heat the capsule to such a degree that it becomes painful to the hand. If there are any brown specks in the residue the heat has been excessive. The residue is then dissolved in distilled water and the acidity is determined again. The difference between the second and the third determination shows the volatile acids. The difference between the first and the second is due to $CO_2$.

**Contributions to Kjeldahl's Process for the Determination of Nitrogen.**—Carl Arnold and Konrad Wedemeyer.—The authors examine in succession the action of different oxidising agents; the behaviour of substances which contain nitrogen in ring-formed combination; the behaviour of compounds which contain groups connected by atoms of nitrogen; the behaviour of some other nitrogen compounds; comparative determinations of nitrogen in compounds where it is present as oxides, and new methods for determining the oxides of nitrogen.—*Zeit. fur Anal. Chemie*, xxxi., Part 5.

## MEETINGS FOR THE WEEK.

Monday, 23rd.—Medical, 8.30.
Tuesday, 24th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "The Theory of 'Storiation' in Art," by Hugh Stannus, F.R.I.B.A.
Wednesday, 25th.—Society of Arts, 8. "The Fine Arts in Relation to the Sanitary Condition of our Great Cities," by Wyke Bayliss, P.R.S. Brit. Arts.
—— British Astronomical Association, 5.
—— Geological 8.
Thursday, 26th.—Royal, 4.30.
—— Royal Institution, 3. "Tennyson," by the Rev. Canon Ainger, M.A., LL.D.
—— Institute of Electrical Engineers, 8.
Friday, 27th.—Royal Institution, 9. "The Just-Perceptible Difference," by Francis Galton, F.R.S.
—— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
—— Physical, 5. "Japanese Magic Mirrors," by S. P. Thompson, F.R.S. "The Perception of Colour," by W. F. Stanley, F.G.S. "Recent Determinations of Molecular Refraction and Dispersion," by Dr. J. H. Gladstone, F.R.S.
Saturday, 28th.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

## TO CORRESPONDENTS.

*W. Rushby.*—(1) Prof. Mallet's Address on the Life and Work of Stas will be published in the Chemical News in the course of a few months. (2) See the Chemical News, vol. lxiv., p. 108. (3) *Proc. R. S.* (4) It publishes a monthly journal.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1731.

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## THE RATE OF EXPLOSION IN GASES.*

By HAROLD B. DIXON, M.A., F.R.S.,
Professor of Chemistry in the Owens College, Manchester.

1. Berthelot's measurements of the rates of explosion of a number of gaseous mixtures have been confirmed. The rate of the explosion wave for each mixture is constant. It is independent of the diameter of the tube above a certain limit.

2. The rate is not absolutely independent of the initial temperature and pressure of the gases. With rise of temperature the rate falls; with rise of pressure the rate increases; but above a certain *crucial pressure* variations in pressure appear to have no effect.

3. In the explosion of carbonic oxide and oxygen in a long tube, the presence of steam has a marked effect on the rate. From measurements of the rate of explosion with different quantities of steam, the conclusion is drawn that at the high temperature of the explosion wave, as well as in ordinary combustion, the oxidation of the carbonic oxide is effected by the interaction of the steam.

4. Inert gases are found to retard the explosion wave according to their volume and density. Within wide limits an excess of one of the combustible gases has the same retarding effect as an inert gas (of the same volume and density) which can take no part in the reaction.

5. Measurements of the rate of explosion can be employed for determining the course of some chemical changes.

In the explosion of a volatile carbon compound with oxygen, the gaseous carbon appears to burn first to carbonic oxide, and afterwards, if oxygen is present in excess, the carbonic oxide first formed burns to carbonic acid.

6. The theory proposed by Berthelot—that in the explosion wave the flame travels at the mean velocity of the products of combustion—although in agreement with the rates observed in a certain number of cases, does not account for the velocities found in other gaseous mixtures.

7. It seems probable that in the explosion wave—

(1) The gases are heated at *constant volume*, and not at *constant pressure*;

(2) Each layer of gas is raised in temperature *before* being burnt;

(3) The wave is propagated not only by the movements of the burnt molecules, but also by those of the heated but yet unburnt molecules;

(4) When the permanent volume of the gases is changed in the chemical reaction, an alteration of temperature is thereby caused which affects the velocity of the wave.

8. In a gas, of the mean density and temperature calculated on these assumptions, a sound wave would travel at a velocity which nearly agrees with the observed rate of explosion in those cases where the products of combustion are perfect gases.

9. With mixtures in which steam is formed, the rate of explosion falls below the calculated rate of the sound wave. But when such mixtures are largely diluted with an inert gas, the calculated and found velocities coincide. It seems reasonable to suppose that at the higher temperatures the lowering of the rate of explosion is brought about by the dissociation of the steam, or by an increase in its specific heat, or by both these causes.

10. The propagation of the explosion wave in gases must be accompanied by a very high pressure lasting for a very short time. The experiments of MM. Mallard and Le Chatelier, as well as the author's, show the presence of these fugitive pressures. It is possible that data for calculating the pressures produced may be derived from a knowledge of the densities of the unburnt gases and of their rates of explosion.

---

* Abstract of the Bakerian Lecture read before the Royal Society, January 19, 1893.

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### ON A

## NEW BOILING AND DISTILLING VESSEL.*

By THEOD. FREDERKING.

An invention has lately been made in Germany which is likely to become of great importance for the whole chemical industry, for breweries, for manufacturers of food-stuffs, &c. This invention, which has been patented in all countries, relates to a boiling vessel which does not come into contact with the fire, and in which any combustible, explosive, and similar matter, may be boiled, vaporised, melted, or distilled, which requires to be boiled at a precisely fixed temperature, and which possesses a high boiling or melting point.

The peculiarity of the vessel is, that pipes of great strength are cast into its massive metal walls, so that the heat introduced into the pipes is rapidly communicated to the good conducting wall and to the contents of the vessel. The pipes may be so thick-walled (for instance, Perkin's pipes) as to bear any required pressure, the walls of the vessel being consequently entirely free from the pressure of the heating medium. By these means, the steam pressure, instead of being limited to three atmospheres, as formerly, may be increased to any degree without danger, so that, for instance, with an additional pressure in the steam boiler of six, eight, or ten atmospheres, a boiling temperature of 150°, 160°, or 180° C. may be obtained.

Higher temperatures than those which can be obtained by steam are reached in a simple way by hot-water heating. For this purpose an apparatus of Perkin's or other similar pipes, situated in a suitable stove, is connected with the pipes in the walls of the vessel into a closed pipe system. Distilled or condensation water filled into the pipes will circulate through the pipe system, taking up heat in the stove and transmitting it to the massive walls of the vessel and to the contents of the latter. As water cannot evaporate in a closed conduit, a temperature of from 350° to 400° C. can be reached easily and without inconvenience. These boiling arrangements, being neither steam nor hot water, are not subject to governmental supervision, for as the strength of the pipes is tried up to 300 atmospheres, and as they contain but a small quantity of water, as moreover the walls of the vessel are free from pressure, and as the stove may be erected at any distance from the boiling vessel, there is no danger in working.

As may be foreseen, the vessel worked by steam should be quickly adopted in breweries for the coppers, because the great losses of fuel, as well as of the copper burning through when they are heated over fire, make the introduction of steam boiling very desirable, and because the deficiencies connected with the former way of boiling by steam in double walled vessels with a low steam pressure are entirely done away with. Moreover, the boiling of pitch is also advantageously effected with patent vessels and water heating, on account of the former's great danger of fire. As the stove may be placed in any side room, danger of fire in the pitch-boiling house will be out of question.

The steam boiling vessels are also employed with advantage for the melting of tallow or grease; the requi-

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* D. R. P. No. 63315.

site temperature of about 160° to 170° being easily obtained through steam of eight or ten atmospheres additional pressure introduced into the walls of the vessel. By the employment of a steam boiler, specially erected for the melting, the working may be arranged to be very profitable.

The patent vessels with hot water arrangement are of great importance—for instance, for the manufacturing of printer's inks, oil cloth, &c., for the boiling of linseed oil, and for all industries working with resins, pitch, tar, distillation of coal, &c. These few examples are sufficient to show what important part the new boiling vessel is to play in industry, and we will only still mention the melting of sulphur (which may be effected in the patent vessel with steam at four atmospheres additional pressure, without danger and in less time than over fire), the manufacture of soap and candles, perfumery, essential oils, colours (for instance, boiling vessel constructed as autoclaves), and the dye-works. At the same time, conscious that this does not by any means exhaust the availableness of the apparatus, we may even say that it will soon be adopted in all industries where boiling, vaporising, melting, or distilling is done.

## ON THE
## PROBABLE SPECTRUM OF SULPHUR.

By JOSEPH SWEETMAN AMES.

While pursuing in the winter of 1889 some investigations on the spectrum of hydrogen, I was surprised to find on several of my photographic plates lines which evidently had no connection with hydrogen. These lines formed most beautiful series, bearing a striking resemblance to the B group of the solar spectrum. In some cases the series overlap, in others they are perfectly distinct. The head of each series is towards the shorter wave-lengths, and the lines are generally grouped in pairs. There is one very faint series of pairs beginning about wave-length 2860; at wave-length 3020 a series of single lines begins; from wave-length 3065 to wave-length 3200 there is almost hopeless confusion of overlapping series, most of the lines being strong and sharp; and at wave-length 3200 begins a series of at least twelve pairs, which in its intensity and in all its physical properties is remarkably like the B group.

My reason for believing these series to belong to the spectrum of sulphur are largely negative ones. The plates on which they appeared were taken consecutively on the same day. Since then I have tried to secure the same or similar conditions; but not once have I found a trace of the lines. I was using vacuum tubes containing large aluminium electrodes; and the hydrogen was admitted to the tubes over a mercury trap. Plugs of sulphur, blocked by glass wool, were interposed in the connecting tubes to stop the mercury vapour. It sometimes happened that the hydrogen would bubble up through the mercury trap faster than was desirable; and it is perfectly possible that with the mercury vapour, traces of which could always be detected in my tubes, some particles of sulphur were carried through. The only impurity detected in my tubes was mercury. Traces of water vapour always linger on the walls of vacuum tubes, but its spectrum is known. I have compared these new lines with all the spectra at my disposal, and can find no agreement. The fact that these lines form series so wonderfully like the B group, which is due to oxygen, is an argument, however faint, that they may belong to sulphur, since oxygen and sulphur are so closely connected chemically.

Being unable to convince myself that the spectrum which I obtained was really due to sulphur, I have never measured my plates carefully. I publish this note now only in the hope that some investigator may be able to succeed better than I in securing the necessary conditions for repeating my observations.—*Astronomy and Astro-Physics*, January 1893.

## SOME REMARKS ON THE EXAMINATION OF THE RARE GADOLINITE EARTHS, AND IN PARTICULAR ON DETERMINING THE EQUIVALENTS OF THESE EARTHS BY CONVERTING THE OXIDE INTO THE SULPHATE.

By GERHARD KRÜSS.

(Concluded from p. 33).

For the complete removal of the excess of sulphuric acid without the formation of basic sulphate, the crucible is placed above the flame, 3 c.m. in height, of an ordinary Bunsen burner, provided with a chimney so that the point of the flame is at the distance of 8 c.m. from the bottom of the crucible. After one hour the flame is raised to 8 c.m. After six hours the crucible is allowed to cool for one hour in the exsiccator and weighed. It is then heated again for six hours, again weighed, &c. The second weighing generally agrees with the former except for the slight increase of weight which takes place during weighing. If this is not the case with larger quantities, the third or fourth weighing proves constant.

In any case already in the third or fourth weighing, the scale should be loaded with the same weights used in the first weighing, or rather less, before the crucible with sulphate is removed from the phosphoric anhydride desiccator to the balance. The same procedure is also to be employed in taking the constant weight of the earths after repeated ignition.

A quantity of 0·2 grm. oxide is sufficient for an accurate result, and it is not advisable to use more than 0·5 grm. earth for determining the equivalent, as otherwise the sulphate formed can only be brought to a constant weight after a very long time. For the conversion of oxide into sulphate porcelain crucibles were preferred to those of platinum. Independently of the considerable number of crucibles requisite for the simultaneous performance of ten to fifteen analyses, the substance may be more easily heated *uniformly* to several hundred degrees in a porcelain crucible than in one of platinum, since platinum conducts away the heat more quickly from the hottest part of the bottom. It might be objected against the use of porcelain that during the conversion of the oxide into sulphate, by fuming off the free acid, the glaze of the crucible might be perhaps attacked, and thereby the weight of the crucible might vary during the experiment.

Only in single cases was the glaze of the crucible found distinctly corroded after being once used, which was accompanied by a considerable loss of weight of the crucible. In such case, not merely the determination in question, but the crucible itself was at once rejected. But if the weight of the crucible varied in the course of the first experiment only by $\frac{1}{10}$ or $\frac{2}{10}$ of a m.grm., the crucible could be used for an extensive series of determinations. In order to show the permanence of the crucibles used, the author gives the weights which some of them showed after repeated ignitions.

In order to show the stable nature of the crucibles employed, I append the weights of some of them after each ignition before a new determination. The numbers show sufficiently the suitableness of porcelain crucibles for the purpose in question.

The following data show, in opposition to the experiments of G. H. Bailey, that the rare earths may be quantitatively converted into sulphate whether they are strongly or feebly basic, and that in the process of driving off the excess of sulphuric acid, we can arrive at a point where the weight is constant. This may be seen from the following results, which show the weights of crucible + earthy sulphates after repeated ignitions—each time for six hours—and weighing.

| Ytterbium sulphate. | Erbium sulphates. | | Yttrium sulphate. |
|---|---|---|---|
| $\overset{\text{III}}{\text{R}}$ = 172·03 | $\overset{\text{III}}{\text{R}}$ = 169·6 | $\overset{\text{III}}{\text{R}}$ = 165·43 | $\overset{\text{III}}{\text{R}}$ = 93·72 |
| 8·6494 | 7·6125 | 6·9538 | 6·2906 |
| 8·6496 | 7·6122 | 6·9536 | 6·2908 |
| 8·6496 | 7·6122 | 6·9537 | 6·2908 |
| 8·6495 | 7·6123 | 6·9536 | 6·2907 |

| Didymium sulphates. | | |
|---|---|---|
| $\overset{\text{III}}{\text{R}}$ = 140·2 | $\overset{\text{III}}{\text{R}}$ = 145·17 | $\overset{\text{III}}{\text{R}}$ = 144·53 |
| 7·8589 | 11·2735 | 13·2030 |
| 7 8585 | 11·2731 | 13·2026 |
| 7·8583 | 11·2735 | 13·2029 |
| 7·8586 | 11·2723 | 13·2026 |
| | 11·2725 | 13·2027 |

The residual sulphates, in spite of the prolonged heating above the incipient boiling-point of sulphuric acid, did not give off any more acid. They also gave clear solutions in water. Hence, according to the accepted view, they were neutral sulphates. Still, it might be objected that a basic earthy sulphate may possibly be slightly soluble in a concentrated solution of neutral sulphate, and that the observation of the perfect solubility of the residue, after the ignition, does not justify the conclusion of the absence of basic salt.

If during the expulsion of the excessive sulphuric acid there has been formed in part a basic sulphate, it must seem strange that on further ignition to the same temperature this decomposition is suddenly arrested, whilst in such decompositions the weight of the substance approaches asymptotically to a constant limit value. But in this case the weight of the sulphate can by no means remain unchanged at two different temperatures. At a higher temperature the decomposition must certainly continue if the formation of a basic salt has begun at a lower temperature. The following experiments show the behaviour of the sulphates in this direction. The materials employed were:—

| | | No. 1. Yttria—almost white. | No. 2. Ytterbia—snow-white. | No. 3. Terbiniferous yttria—yellow. |
|---|---|---|---|---|
| Weight of crucible | = | 7·4856 | 6·7979 | 8·1175 |
| D. + oxide .. .. | = | 7·9153 | 7·3603 | 8·4007 |
| Crucible + sulphate :— | | | | |
| I. | | 8·5282 | 7·613 | 8·6800 |
| | | 8·52 | 7·610 | 8·6779 |
| | | 8·48 | 7·6083 | 8·6768 |
| II. | | 8·3643 | 7·6066 | 8·6765 |
| | | 8·3615 | 7·6064 | 8·6758 |
| | | 8·361 | 7·6063 | 8·6757 |
| | | 8·3578 | 7·6061 | 8·6759 |
| | | 8·3578 | 7·6060 | |
| | | 8·3582 | | |
| III. | | 8·3568 | 7·6059 | 8·6757 |
| | | 8·3572 | 7·6061 | 8·6755 |
| | | 8·3568 | 7·6060 | 8·6756 |
| IV. | | 8·3568 | 7·6060 | |
| | | 8·3570 | 7·6059 | |

The numbers under I. represent the weights of the crucibles + sulphates after each eight hours' heating on the iron plate with the triple burner. In II. each was heated for eight hours with a direct Bunsen flame 3·8 c.m. high (regulated with a precision cock), so that its point was at the distance of 8·6 c.m. from the bottom of the crucible. Neither lead nor tin fused so that the temperature was evidently below 228°, and yet constancy was obtained for specimens 2 and 3.

In III. the crucibles were heated for eight hours with a Bunsen flame 9 c.m. in height, the point of which was at the distance of 4 c.m. from the bottom of the crucible. Lead melted at this temperature, so that the heat was raised to 325° or higher. In IV. the flame, 11 c.m. in height, reached almost to the bottom of the crucible. Zinc, or antimony, did not melt at this temperature, so that it must have been below 415°. It may, approximately, have been from 370° to 380°. It must have been between 325° and 415°, and indeed considerably above the melting-point of lead (325°), as this had been already exceeded in III.

Except in experiment No. 1 the earthy sulphates had given off all free acid completely below 228°, even if only on prolonged heating. If we consider the sulphate of the feeblest base ytterbium sulphate (experiment No. 2), which must be most readily decomposed by heat, and which reached a constant weight even below 228°, after being heated for forty hours up to 380°, retained the same weight.

The determination of the equivalents of the gadolinite earths, by converting the oxide into anhydrous sulphate, can therefore be conducted with perfect exactitude if the fuming off the excess of free acid is cautiously effected by keeping the crucibles first at from 200° to 220°, and then gradually heating above 290°—the point at which sulphuric acid begins to boil—up to about 350°. In this manner we obtain neutral earthy sulphates free from uncombined sulphuric acid and from basic sulphates. If the conditions of the experiment are regulated by means of precision gas-cocks, the conversion of the earths into sulphates can be effected simultaneously in a great number of determinations without the necessity for unbroken attention. If the earthy sulphates are heated above the melting-point of antimony, the sulphate is gradually decomposed, with continuous loss of weight.

Finally, it must again be pointed out, that the excess of sulphuric acid must be driven off with the least possible interruption, and that the contents of the crucible must not be allowed to stand in moist air before the end of the operation. In such cases the salt tumefies, and on further heating is found in a state of much finer division, so that the crucible is more completely filled; the contents of the crucible cannot then be so uniformly heated as when smaller quantities of sulphate cover the bottom in the form of crusts.

In such a finely-divided and more unfavourable state was the yttria No. 1, mentioned in the above table. Hence this sulphate did not reach a constant weight until later. It is equally unfavourable to use more than 0·5 grm. of earth for the experiment, as a longer time is required before the weight becomes constant. According to the above example, 1·3073 grms. of a terbiferous yttria after conversion into sulphate, yielded exactly the same $\overset{\text{III}}{\text{R}}$ of 99·6 for this yttria material as 0·2832 grm. of the same oxide in another determination. Determinations of equivalents, with from 0·2 to 0·4 grm. of the earth in considerable time, and at the same time with equally distinct results.

The above method for determining the combining weights of the earths is perfectly unobjectionable under the conditions laid down. It was applied in this manner in the researches on erbium, holmium, and terbium (to be given below), as well as in new methods for separating the earths.

Before reporting the latter, I wish to insert a brief conspectus of the methods hitherto employed for separating and isolating the yttrium and cerium earths. The conspectus has been drawn up by Dr. A. Loose. In our more extensive inorganic text-books, and in some general collected works on chemistry, there may be found in part excellent monographs of the rare earths. But such a conspectus may now be made considerably more complete, especially as of late many researches have been made in this department. Perhaps the following conspectus, drawn up as briefly as possible, and characterised by its modified arrangement, may be found to facilitate a view of previous researches in this direction, and to render references to the bibliography of the subject more easy.

## THE CONSTITUTION OF MAGNETIC OXIDES.*

By STEPHEN H. EMMENS.

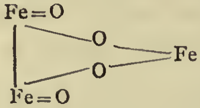
In the process of nickel manufacture practised by the Emmens Metal Company at Youngwood, Westmoreland Co., Pa., the metal is granulated by pouring it, when molten, into water. This operation usually proceeds quietly and without interruption; but occasionally sharp explosions take place as the metal touches the surface of the water. Investigation into the conditions of these explosions has shown that the phenomenon is always accompanied by a more or less oxidised state of the molten metal; that is to say, the nickel ore has not been completely reduced to metal in the operations preceding that of granulation.

It is also noticed that when no explosions occur, and when the molten metal sinks quietly to the bottom of the granulating vessel, bubbles of gas rise to the surface of the water and burn there with a blue flame.

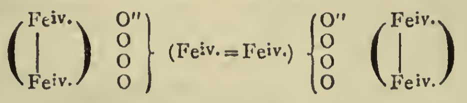
Inasmuch, then, as the fully reduced metal appears to decompose water, and as the partially reduced metal causes an explosion when coming into contact with water, it would seem that, in the latter case, the presumably homogeneous mass of molten metal consists partly of molecules of free nickel which liberate hydrogen from the water, and partly of molecules of nickel oxide which supply oxygen to at once combine explosively with the hydrogen.

This explanation, namely, that an oxide of nickel probably exists in which the metal is partly metallic and partly oxidised, suggests an analogous explanation of an analogous phenomenon, *i.e.*, the magnetic character of certain oxides.

Chemists have hitherto been, for the most part, agreed in considering the magnetic oxide of iron, $Fe_3O_4$, as being, to quote Mendeleeff ("Principles of Chemistry," translated by Kamensky and Greenaway), "composed of ferrous and ferric oxides." Indeed, Mendeleeff specifically speaks of "the so called magnetic oxide containing atomic quantities of the suboxide and oxide, viz., FeO, $Fe_2O_3 = Fe_3O_4$." And the new edition of "Watts' Dictionary" says "$Fe_3O_4$ may be regarded as FeO, $Fe_2O_3$"; while the old edition (Second Supplement) gives the following graphic formula for $Fe_3O_4$:—



in which ferrous (bivalent) iron is represented as forming an unsaturated compound, $FeO_2$, which is united with an unsaturated compound, $Fe_2O_4$, of ferric (in this case quadrivalent) iron. Drechsel, on the other hand ("Introduction to the Study of Chemical Reactions," translated by Merrill), admits $Fe_3O_4$, or rather $Fe_6O_8$, to a place among the true iron oxides, and pictures its constitution as follows:—



contending that iron is quadrivalent only, and not at any time either bivalent or trivalent.

None of these views throw any light upon the most remarkable property of $Fe_3O_4$; that is to say, they show no reason why it should be much more magnetic than its fellow oxides, and especially than the protoxide, FeO, which contains a larger percentage of the metal. The question, therefore, of the true molecular constitution of magnetic iron oxide may be regarded as being still an open one; unless, indeed, there be any considerations of paramount importance already advanced for compelling the recognition of FeO,$Fe_2O_3$. If we search for such reasons we shall find them to be two in number, viz.:—

1. *The Argument from Isomorphism.*— Magnetite ($Fe_3O_4$) is found in nature as a mineral isomorphous with spinel ($MgAl_2O_4$), gahnite ($ZnAl_2O_4$), zeilanite ($FeAl_2O_4$), franklinite ($ZnFe_2O_4$), and chromite ($FeCr_2O_4$). It is assumed that spinel must contain MgO, that gahnite and franklinite must contain ZnO, that zeilanite must contain $Al_2O_3$, that chromite must contain $Cr_2O_3$, and that therefore the former three must also contain $Fe_2O_3$ and the latter two FeO. But if these assumed necessities do not in point of fact exist, the argument falls to the ground; and as no attempt is made to prove their existence we are justified in treating the argument as of no weight,—a very frequent thing in cases of isomorphism.

2. *The Argument from Solution.*—If $Fe_3O_4$ be dissolved by acids, ferrous and ferric salts are found in solution. This is held as proof that $Fe_3O_4$ consists of FeO and $Fe_2O_3$. But if Fe be dissolved by $H_2SO_4$ and form $FeSO_4$,Aq, no one dreams of declaring that Fe must have contained FeO. Solution certainly implies a degree of molecular disaggregation that admits of re-arrangement; and so far from the presumption being in favour of a continuance of pre-existing molecular structure, it is obviously the reverse.

Seeing, then, that no good reason exists for regarding $Fe_3O_4$ as FeO,$Fe_2O_3$, it may be well to enquire whether any valid arguments can be advanced *against such a view.*

First, the compound $Fe_2O_3$ is of a very stable character, and is, with reason, regarded as "saturated." If, then, it be linked to FeO, this can only be by means of some hitherto unknown and unrecognised affinity invented or imagined for the occasion.

Secondly, FeO is of a very unstable character; so much so, indeed, that the ordinary assumption of its being "saturated" appears to have very slender foundation. Its combinations with $Fe_2O_3$ by means of the mysterious affinity above mentioned should not, apparently, interfere with its proneness to oxidation; and the compound FeO,$Fe_2O_3$ should readily change into $2Fe_2O_3$, whereas, in point of fact, $Fe_3O_4$ is so stable and unoxidisable that it is artificially produced on the surface of iron (*i.e.*, the "Barff" and "Bower" processes) as a durable coating for the purpose of preventing that metal from rusting.

Thirdly, FeO is somewhat magnetic, but $Fe_2O_3$ is very slightly so, if at all. According to Becquerel, $Fe_2O_3$ is diamagnetic, and this is also stated by Mendeleeff and other authorities; though Plucker gives the specific magnetism of specular iron ore as 533 compared with 40227 for $Fe_3O_4$, and Sidot (*Compt. Rend.*, lxvii., 175) has obtained an oxide exhibiting magnetic polarity by heating ferric oxide in an earthen tube placed in the magnetic meridian to a temperature not sufficient to fuse the oxide. A. Frenzel also (*Jahr. f. Min.*, 1874, 685) obtained small rhombohedrons of iron glance, slightly magnetic, by igniting a precipitate of ferric hydrate; and Malaguti (*Ann. Chim. Phys.*, [3], lxix, 214) states that a magnetic variety of $Fe_2O_3$ exists. These discrepant assertions may perhaps be caused by the fact that $Fe_2O_3$ when strongly heated gives off oxygen, and is partially converted into $Fe_3O_4$. But be this as it may, the very slightly magnetic character of both FeO and $Fe_2O_3$ is as incontestable as is the highly magnetic character of $Fe_3O_4$. And as magnetism is conceded to be a physical property, dependent in some unknown way upon the molecular structure of bodies, the inference is irresistible that the molecules of iron and oxygen in $Fe_3O_4$ cannot be arranged

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* *Journal of Analytical and Applied Chemistry*, October, 1892.

in two groups, one of which has the structure of FeO and the other that of $Fe_2O_3$.

Fourthly, neither the hydrate of FeO nor that of $Fe_2O_3$ is magnetic. But the hydrate of $Fe_3O_4$ is attractable by the magnet, both when in the liquid from which it is precipitated and when in a dry state. Here, again, it seems idle to suppose that $Fe_3O_4$ exists as a combination of FeO and $Fe_2O_3$.

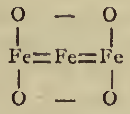
Fifthly, Lefort (*Compt. Rend*, lxix., 179) has succeeded in forming a definite salt by dissolving $Fe_3O_4$ in $H_2SO_4$, and evaporating the solution over $H_2SO_4$. This sulphate has the composition $Fe_3O_4,6SO_3,15H_2O$. But FeO combines with one molecule of $SO_3$ and $Fe_2O_3$ with three molecules of $SO_3$; so that the mixture $FeO+Fe_2O_3$ will combine with $4SO_3$. The combining power of $Fe_3O_4$ is therefore very different from that of $FeO,Fe_2O_3$.

Sixthly, if $Fe_3O_4$ be composed of a molecule of FeO united to one of $Fe_2O_3$, it would seem that only one grouping is possible, and that no isomer of the normal $Fe_3O_4$ can exist. But according to Moissan (*Ann. Chim. Phys.*, [5], xxi., 223) and Berthelot (*Ann. Chim. Phys.*, [5], xxiii., 118), two varieties of $Fe_3O_4$ exist, having distinct specific gravities, different solubilities in $HNO_3$, and different behaviours when exposed to heat. It follows that $Fe_3O_4$ cannot have the constitution $FeO,Fe_2O_3$; unless, indeed, the isomerism be regarded as due to the presence of two varieties of $Fe_2O_3$.

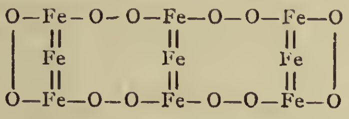
Having now shown that no good reason exists for regarding $Fe_3O_4$ as being $FeO,Fe_2O_3$, and that many good reasons exist against such a view, it remains for me to point out that another view of the molecular constitution is possible and preferable.

Let us, with Drechsel, F. W. Clarke, and some other chemists, regard iron as being a quadrivalent element, and let us dismiss the imaginary *ferrosum* and *ferricum* from our minds. Let us also consider oxygen as being virtually bivalent. And let us recognise the fact of the magnetic property of iron being impaired and well nigh destroyed by the union of the metal with oxygen; a fact which leads us to conclude that in any strongly magnetic oxide of iron some part at least of the metallic molecules must exist uncombined save with iron. The problem then arises whether any possible grouping of the molecules in $Fe_3O_4$ can comply with the requirements thus premised.

I submit that the following graphic formula is a solution of the problem, viz:—



Here each molecule of Fe is quadrivalent, and each molecule of O is bivalent. One-third of the iron, moreover, is uncombined save with iron, and is, therefore, fully magnetic. We also see that a polymeric form is possible, viz:—



and this may well account for there being two varieties of magnetic oxide, in both of which the proportions of iron and oxygen are as $Fe_3$ to $O_4$.

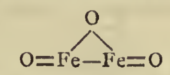
The slightly magnetic character of the protoxide may, I think, be shown by adopting the following formula:—

$$=Fe=O$$

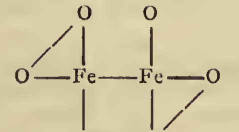
in which the iron molecule is not fully linked, and is, therefore, free to combine with another molecule of FeO, thus,—

$$O=Fe=Fe=O,$$

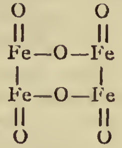
forming a somewhat magnetic body, which is easily oxidised into the less magnetic ferric oxide, $Fe_2O_3$,—



and this, by further oxidation, becomes ferric anhydride, $FeO_3$, or $Fe_2O_6$—



It will be observed that the suggested constitution of $Fe_2O_3$ also admits of a polymeric variation, viz:—



and in accordance with this view it may be mentioned that two varieties of ferric oxide as well as of $Fe_3O_4$ are known. Indeed, as Mendeleeff very justly observes (*loc. cit.*, p. 324), "all phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, lead hydroxide, &c., is polymerised, that the composition is represented by $(Fe_2O_3)_n$."

In conclusion I would add that in the foregoing observations I have employed the concepts of molecule, valency, and the like merely as customary useful aids to such an understanding and explanation of chemical and physical relations and phenomena as is possible in the present limited condition of our knowledge, and not as representing the esoteric facts of nature.

## CHEMICAL ACTION BETWEEN SOLIDS.[*]

By WILLIAM HALLOCK.

IN a note on a new method of forming alloys published some time ago (W. Hallock, *Zeit. Phys. Chem.*, ii., 1888, p. 6; *Science*, xi., 1888, p. 265), I suggested some additional experiments which I intended to make, and I now give the results thus far obtained. Unfortunately, other work prevents my continuing the investigation at present.

Inasmuch as the method and principle[†] seemed well established where metals were used to produce alloys, an attempt was made to include some chemical reactions in the list. The most natural cases were the freezing mixtures where solid reagents are used. In order to surely have both constituents in a decidedly solid state, the experiments were performed in a vessel cooled to a temperature of −10° or 12° C., care being always taken to leave the reagents in the vessel long enough for them to assume a temperature decidedly below zero Centigrade. Under these conditions a crystal of rock salt (NaCl) and a piece of clean, dry ice, were gently brought in contact, lying side by side on a watch-glass. Of course the result

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[*] This paper was read in part before the Phil. Soc. of Washington, D.C., Oct. 13, 1888, and appeared in full in the *Amer. Jour. Sci.*, vol. xxxvii., 1889, p. 402.

[†] O. Lehmann (*Wiedemann Ann.*, xxiv., 1885, p. 5), suggested the theoretical possibility of producing an alloy in this way. I had overlooked his paper until recently. Mr. Lehmann, however, evidently did not consider it possible to fulfil the necessary conditions and did not try the experiment.

was the solution of salt, but old as this experiment may be, it appears here in a new connection, as an example of the union of two solids below the melting-point of either, but above that of the product. The piece of ice was frozen to the glass, and during the operation the crystal was drawn several millimetres across the glass, doubtless by capillarity, as the solution ran out at the bottom of the surface of contact as fast as it formed, the attraction being sufficient to move a crystal several grms. in weight.

Similar experiments were performed with sodium and potassium, nitrate potassium, calcium and ammonium chloride, and sodium and potassium hydrate, with a similar result in all cases. These are all well-known results, but wherein do they differ from the new method of forming alloys? This question suggests another. Are the metals combining to form an alloy in the new way a freezing mixture? A thorough investigation of the question would require more complicated experiments than I had time to perform. One test, however, is very simple, that with potassium and sodium.

Into a small porcelain crucible weighing 15 grms. and containing about an equal weight of petroleum, were placed pieces of the two metals, about 3 grms. of each. One junction of a thermo-element was forced into the piece of potassium and gave its temperature accurately. After the whole had assumed the room temperature, clean faces of the two metals were brought into contact, the liquefaction began, and *the temperature immediately fell.* It required about two hours to complete the liquefaction, and about one and a half hours to attain the minimum of temperature. No precautions were taken to prevent the calorimeter taking up heat from its surroundings, and no doubt, it absorbed considerably in the long time, and yet the maximum fall in temperature amounted to 2·4° C. —very large considering the small weight of the reagents compared with the calorimeter. Thus it appears that sodium and potassium are, under such circumstances, a "freezing mixture," and analogy at least would lead one to believe that other alloys also absorb heat in their formation; but future experiment must decide the point.

In the cool vessel above described, a piece of sodium or potassium was placed upon a piece of dry ice; almost instantly the reaction commenced and proceeded vigorously. It is, however, scarcely safe to consider this a case of chemical action between solids, because the reaction is probably as follows: The vapour from the ice attacks the metal, forming the hydrate which unites with other ice, forming a solution, which is then further acted upon by the metal, and in the whole process heat is generated sufficient to raise the temperature of the reagents very considerably. Perhaps in the other freezing mixtures, ice and salt, &c., it is the vapour of the water or ice which initiates the reaction.

In view of these and other considerations, the idea is evident that perhaps many substances have a slight vapour tension at temperatures considerably below their melting-points, and are surrounded by a thin atmosphere of their own vapour over their clean surfaces, and it is only necessary to bring two such atmospheres to interpenetration in order to initiate the reaction which will then continue, provided the product (liquid or gas) escapes easily and does not clog the operation. In very many cases substances are found to give off a vapour below their melting-point, and it is natural to suppose that there is a film of that vapour over the surface of the body, as there is a layer of saturated air over water. The mechanical theory of the composition of matter lends plausibility to the above suggestion. If these considerations are correct they foretell the regelation of substances like camphor and ice, without any pressure whatever. That loose pieces of camphor will become welded together by simple contact is well known. The operation appears to me thus:—In an irregular mass of camphor in an atmosphere of camphor vapour, there is a constant interchange of state for the molecules at the surfaces of the solid, molecules previously solid are getting too far off and becoming gas, and molecules previously gas are beating upon the solid and staying there; thus the state of equilibrium is when, as a whole, there are as many molecules which fly off and become gas as fly on and become solid. On a projecting point of the solid the chances are in favour of more flying off than on; in a re-entrant angle the reverse is true. Theoretically, then, the piece ought ultimately to become a sphere, not only by the rounding down of the corners, but by the building up of the flat or re-entrant sides. That the corners do round off all know. If this is all true we only need to bring the two pieces together and consider them as one, and the crack between them as a re-entrant angle, and the union is brought about as above indicated. If in the above the word liquid be substituted for vapour or gas, the explanation will apply to the regelation of ice in water at 0° C.

We may go even further and predict a uniting without actual contact, and this prediction has been experimentally demonstrated in the case of ice and water. A large rough block of ice (about fifteen pounds) was sawed nearly in two, the slit washed out and all the fine pieces removed. In this way it was possible to hold two plane surfaces of ice parallel and near each other (1 to 2 m.m.) without danger of actual contact. Into the outer edge of the saw cut a cotton wick was pressed, thus isolating the space between the faces from the outside and preventing any currents from circulating through the crack. The whole block was then placed in water at zero and inclosed in non-conducting cases and left for twenty-five to thirty hours. This experiment was tried three times, and each time a freezing across the space had taken place. The whole space was not filled, but in numerous places, notably along just inside the wicking and up from the bottom of the cut. No doubt the regelation would have gone further if the experiment could have been continued longer. The melting of the whole block puts an end to each experiment. As these experiment were performed in summer, there is scarcely a possibility that the ice was colder than 0° C.

Inasmuch as there appears to be an increasing inclination to regard solutions and alloys as chemical compounds, it seems justifiable to speak of the action according to the alloy law as chemical. On the other hand, there are some cases which at first appear as chemical action between solids, which upon closer investigation can be explained on a simpler assumption.

For example, Mr. W. Spring (*Zeit. Phys. Chemie*, ii., 1888, p. 536), in a recent paper on this subject, cites three particular cases as being chemical action between solids, the union of copper and sulphur, the reaction between copper and mercuric chloride, and between potassium nitrate and sodium acetate.

The formation of the sulphide of copper and other sulphides was accomplished by Mr. Spring by compression of the elements. But it is not even necessary that the sulphur and copper be in contact. I have made the sulphide at ordinary temperatures with the two an inch apart, and a wad of cotton in the tube between them. It is simply the *vapour* of sulphur which attacks the copper. That sulphur gives off a perceptible vapour at ordinary temperatures, especially *in vacuo*, is a fact anyone can easily demonstrate. The case of the copper and mercuric chloride is precisely the same. The *vapour* of the chloride will go through a whole tube past cotton wads and attack the copper, or colour potassic iodide. Hence we can scarcely assert that these reactions are between *solid* bodies. The reaction between potassium nitrate and sodium acetate is equally unconvincing. Mr. Spring expected an interchange of bases and acids and left the mixture of the dry fine powders four months in a desiccator to give time for the exchange. On removing them from the desiccator a deliquescence was noticeable, and he therefore concludes that the interchange had taken place, since the original salts do not easily deliquesce; but the product of the reaction (potassium acetate) does.

It appears to me thus:—The moment the powders were brought to the air, the water vapour enters the operation and we have potassium nitrate, water vapour, and sodium acetate, and the result of their mutual interaction is a solution of potassium acetate and sodium nitrate. In fact, if the dry powdered salts are stirred together, in a very few moments deliquescence begins, showing that whatever the reaction it goes on at once, and is a matter of moments and not of months. Thus even this experiment in its present form does not convince us that a chemical exchange took place *before* the water vapour entered the reaction.

The question of chemical action between solids is by no means new, but is being constantly extended. I may say I believe chemical action may take place wherever the product or products are liquid or gaseous even though the reagents are solid, with perhaps the added condition that one or both the reagents be soluble in the liquid produced. If this be true, my new method of forming alloys is but a special case of the above general principle.*—*Bulletin of the United States Geological Survey*, No. 64.

## A METHOD FOR THE QUANTITATIVE SAPARATION OF BARIUM FROM STRONTIUM BY THE ACTION OF AMYL ALCOHOL ON THE BROMIDES.†

By PHILIP E. BROWNING.

The existing methods upon which dependence can be made in the separation of barium from strontium are few in number. Dr. R. Fresenius, in discussing them through several numbers of his journal (*Zeit. Anal. Chemie*, xxix., 20, 143, 413), concludes that the only one which gives perfectly reliable results consists of the precipitation of the barium by a double treatment with ammonium chromate in acetic acid solution.

Having demonstrated the possibility of separating both barium and strontium from calcium by the dehydrating and appropriate solvent action of boiling amyl alcohol on the nitrates (*Amer. Jour. Sci.*, xliii., 50, 314), the possibility of a similar method of separation by the use of suitable salts of barium and strontium seemed worthy of investigation and necessary to complete the series as applied to this group.

In looking about for suitable salts upon which to experiment, the behaviour of the chlorides was suggestive. Barium chloride is completely insoluble in amyl alcohol, while the corresponding strontium salt is somewhat soluble. The possibility of finding strontium bromide more readily soluble than the corresponding chloride seemed worthy of attention. The method of preparation followed was the treatment of the precipitated and thoroughly washed carbonates of barium and strontium with hydrobromic acid (*Proc. Amer. Acad.*, xvii., p. 30), prepared by mixing definite proportions of potassium bromide in solutions with sulphuric acid and water while hot, filtering off the potassium sulphate which separates on cooling, and re-distilling the filtrate until the distillate contains no appreciable trace of sulphuric acid. The standards of the solutions of barium and strontium bromides made in this way were determined by precipitating definite portions, measured and weighed, with sulphuric acid,—the strontium, after the accepted method of adding ethyl alcohol to increase the insolubility, and the barium, after the manner suggested by Dr. F. W. Mar (*Amer. Jour. Sci.*, xli., 288), precipitating with an excess of sulphuric acid in the presence of hydrochloric acid. The mean of closely agreeing results was taken as the standard. Preliminary experiments on the bromides formed in this way gave encouraging results, the barium salt appearing to be almost completely insoluble, while the strontium salt dissolved freely.

The first series of experiments were directed toward a quantitative determination of the solubility of barium bromide in the alcohol. Definite portions of the standardised solution of barium bromide were measured from a burette into counterpoised beakers of about 50 c.m.$^3$ capacity, and weighed as a check on the burette reading. This solution was then evaporated to dryness, and the residue was dissolved in a few drops of water and boiled with 10 c.m.$^3$ of amyl alcohol. The separating bromide was filtered off on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. The crucible containing the bromide was at first dried at 140° to 150° C. in an air-bath after the manner described in the previous papers, and weighed. The unsuccessful attempt to get a constant weight, however, proved the impossibility of weighing as bromide, the weight decreasing rapidly with each successive drying. It was deemed best accordingly to dissolve the bromide from the felt into a beaker placed to receive it, and to precipitate with sulphuric acid in the presence of hydrochloric acid, after the same manner followed in the determinations of the standards. The precipitated sulphate, which in a few minutes settles completely, was filtered off upon the same felt from which the bromide had been dissolved, dried, ignited to low redness, and weighed.

Series I. gives the results of several experiments made after this manner, which show the solubility of the barium salt to be about 0·0013 grm. on the oxide in 10 c.m.$^3$ of amyl alcohol. The filtrate, after boiling with amyl alcohol, was evaporated, and the residue was treated with sulphuric acid and weighed; or the filtrate was precipitated directly by adding sulphuric acid, enough ethyl alcohol being added to secure thorough mixture. The amount of sulphate found agreed uniformly with the loss determined in the residue after boiling. A portion of the salt, which dissolved in the alcohol on being examined before the spectroscope, gave only the green bands characteristic of barium.

Series I.

| | BaO taken. Grm. | BaO found. Grm. | Error. Grm. |
|---|---|---|---|
| 1. | 0·1234 | 0·1222 | 0·0012 – |
| 2. | 0·0824 | 0·0809 | 0·0015 – |
| 3. | 0·0823 | 0·0809 | 0·0014 – |
| 4. | 0·0818 | 0·0803 | 0·0015 – |
| 5. | 0·0733 | 0·0720 | 0·0013 – |

Several methods of treatment were followed to prevent if possible this solubility, such as the addition of a few drops of hydrobromic acid before boiling, of the same after the barium bromide had separated, of a few drops of ethylene dibromide or ethyl bromide at the completion of the boiling, of a few drops of bromine water before boiling, &c. The results of these experiments showed these modifications to be of little or no value.

On boiling the strontium bromide with the alcohol, slight spots separated occasionally, which, on the addition of a drop of hydrobromic acid, went into solution and did not appear on re-boiling. In order to determine the solubility of the strontium bromide in the alcohol, a saturated solution was obtained by boiling an excess of the strontium salt with the alcohol, the salt in a measured portion of 10 c.m.$^3$ was precipitated as sulphate by the addition of ethyl alcohol and sulphuric acid, and weighed. Duplicate determination showed the solubility to be about 0·2 grm. on the oxide in 10 c.m.$^3$ of the alcohol. The mode of procedure for the separation of these elements

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* Experiments endeavouring to produce carbon disulphide from the elements at ordinary temperatures are in hand and give promise of positive results. Also, experiments on the interaction of potassium nitrate and sodium acetate have been started; it will, however, be some time before further results can be given.

† From the *American Journal of Science*, vol. xliv., December, 1892.—Contributions from the Kent Chemical Laboratory of Yale ollege.

was identical with that already described in the case of barium alone, up to the point at which the barium was filtered off, except, of course, the addition at first of a measured and weighed amount of a previously standardised solution of strontium bromide. The strontium was precipitated from the filtrate as sulphate by dilute sulphuric acid, ethyl alcohol being added to secure thorough mixture. These precipitates were generally filtered off upon asbestos felts, and although their gelatinous character delayed the filtration somewhat, the drying and burning of a filter-paper with the possible danger of loss by reduction in the presence of burning paper was avoided.

Series II. gives the results of a single treatment, and it will be seen that there is apparently a slight contamination of the barium by the strontium, which, where the latter is present in large quantities, balances the solubility of the barium (0·0013 grm. on the oxide). Where the amounts of strontium taken are small, the loss of barium due to solubility appears.

SERIES II.

| | BaO taken. Grm. | BaO found. Grm. | Error. Grm. | SrO taken. Grm. | SrO found. Grm. | Error. Grm. |
|---|---|---|---|---|---|---|
| 1. | 0·1228 | 0·1225 | 0·0003 − | 0·1070 | 0·1065 | 0·0005 − |
| 2. | 0·1227 | 0·1231 | 0·0004 + | 0·1074 | 0·1069 | 0·0005 − |
| 3. | 0·1224 | 0·1228 | 0·0004 + | 0·1070 | 0·1067 | 0·0003 − |
| 4. | 0·1217 | 0·1201 | 0·0016 − | 0·0364 | 0·0372 | 0·0008 + |
| 5. | 0·1216 | 0·1222 | 0·0006 + | 0·0133 | 0·1124 | 0·0009 − |
| 6. | 0·0974 | 0·0970 | 0·0004 − | 0·0719 | 0·0721 | 0·0002 + |
| 7. | 0·0971 | 0·0973 | 0·0002 + | 0·0730 | 0·0727 | 0·0003 − |
| 8. | 0·0970 | 0·0971 | 0·0001 + | 0·0718 | 0·0716 | 0·0002 − |
| 9. | 0·0411 | 0·0390 | 0·0021 − | 0·0365 | 0·0385 | 0·0020 + |
| 10. | 0·0243 | 0·0234 | 0·0009 − | 0·1072 | 0·1072 | 0·0000 |

Series III. gives the result of a double treatment. In this series the contaminating effect of the strontium salt disappears entirely, leaving a deficiency of about 0·0025 grm. on the oxide to be added to the barium, and a corresponding amount of sulphate (0·0040 grm.), to be subtracted from the strontium sulphate before calculating it to the condition of the oxide. The manipulation is the same as that outlined for the single treatment, as far as the completion of the first boiling. At this point the amyl alcohol containing most of the strontium in solution was decanted upon a weighed and ignited felt, and collected in a beaker placed to receive it. The residue of barium, with traces of strontium, was then dissolved in a few drops of water, a drop of hydrobromic acid was added, and the boiling was repeated with another portion of 10 c.m.$^3$ of amyl alcohol. Upon reaching the boiling point of the alcohol the beaker was removed, and the barium salt was filtered upon the felt through which the first portion had been decanted, and treated as before described.

SERIES III.

| | BaO taken. Grm. | BaO found. (Correc.) Grm. | Error. Grm. | SrO taken. Grm. | SrO found. (Correc.) Grm. | Error. Grm. |
|---|---|---|---|---|---|---|
| 1. | 0·1212 | 0·1219 | 0·0007 + | 0·1068 | 0·1071 | 0·0003 + |
| 2. | 0·1215 | 0·1219 | 0·0004 + | 0·0358 | 0·0359 | 0·0001 + |
| 3. | 0·1220 | 0·1221 | 0·0001 + | 0·0353 | 0·0347 | 0·0006 − |
| 4. | 0·1212 | 0·1220 | 0·0008 + | 0·0363 | 0·0358 | 0·0005 − |
| 5. | 0·1219 | 0·1221 | 0·0002 + | 0·0361 | 0·0354 | 0·0007 − |
| 6. | 0·1211 | 0·1218 | 0·0007 + | 0·1126 | 0·1116 | 0·0010 − |
| 7. | 0·1319 | 0·1319 | 0·0000 | 0·0577 | 0·0586 | 0·0009 + |
| 8. | 0·0496 | 0·0492 | 0·0004 − | 0·0574 | 0·0579 | 0·0005 + |

The method is rapid, and while the correction to be applied owing to the solubility of the barium salt is large it is so definite that it cannot be objectionable. The author, in conclusion, would express his indebtedness to Prof. F. A. Gooch, of the Kent Laboratory, for the many helpful suggestions received from him bearing upon this investigation.

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# ON GLYCERIN.[*]

By J. LEWKOWITSCH, Ph.D.

At the outset, I wish to disclaim any intention on my part of bringing anything new before you. But having been asked to say something about glycerin—with the manufacture of which I am connected—I thought I might perhaps supplement the remarks made last year by Mr. Siebold and several other gentlemen, in the discussion following Mr. Siebold's paper.

This will be done mostly from the manufacturer's point of view, as manufacturing processes cannot be supposed to be generally known, and it is not at all unlikely that erroneous opinions may be current amongst those not conversant with practical processes used in chemical works.

During the last year it has been repeatedly stated that some samples of glycerin destined for pharmaceutical purposes contained arsenic, a fact which was not unknown to manufacturers, but on which, for very obvious reasons, they did not care to enlighten the consumers. The arsenic in the glycerin owes its existence only to the arsenic contained in the reagents used in the manufacturing process. It has been pointed out by several gentlemen in last year's discussion, that glycerin purified by distillation would not be contaminated by this poisonous substance; although it is but fair to say that Mr. Allen had some doubts about it, still, in the concluding remarks it was distinctly stated that arsenic could be removed by distillation.

This is not so, as the simple fact will show that nowadays all glycerin for pharmaceutical purposes is distilled, nay, even double distilled, glycerin. The times when glycerin was being prepared by other processes of refining have gone by, and a glycerin which had not been purified by steam distillation would be unsaleable for pharmaceutical purposes.

But to remove every doubt, I prepared the substance formed when arsenious acid is dissolved in glycerin, a substance which has been described by Schiff, and later on by Jackson, who apparently overlooked the earlier publication of Schiff. This substance is the arsenious ether of glycerin, $AsO_3(C_3H_5)$. On being heated to 250° C., it decomposes, while arseniuretted hydrogen and other volatile arsenious compounds distil over. At the same temperature glycerin distils also over, and it is quite evident therefore that any arsenic contained in glycerin will distil along with it. The experiments which I carried out could not show any other result.

Arsenic contained in glycerin cannot be removed by distillation, and to my knowledge there is no process known for completely freeing glycerin from arsenic on a practical scale.

Pure glycerin, free from arsenic, can therefore be obtained from such sources only where reagents not contaminated with arsenic are being used. As it has been suggested last year that glycerin emanating from certain processes ought to be rigorously excluded by the Pharmacopœia, I may be allowed here to very briefly review from our point of view the processes used for manufacturing glycerin. The raw materials are exclusively fats and oils which yield on saponification or hydrolysis the glycerin as a by-product.

Glycerin free from arsenic will be obtained in those processes where the fats are hydrolysed by means of water, whether it be used in the liquid state, under high pressure, or as superheated steam. The lime saponification, which is yet largely practised, especially in smaller works, will, as a rule, also yield an arsenic-free glycerin. On the contrary, all glycerin coming from works where the sulphuric acid saponification is practised, will contain arsenic, as the glycerin will extract all the arsenic from the sulphuric acid. There is, however, no doubt that

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[*] British Pharmaceutical Conference, Leeds.

even such glycerin would be pure, as far as arsenic is concerned, if sulphuric acid free from arsenic were used, as it may be prepared from the sulphur obtained by Chance's process.

There is consequently no doubt that there are sources from which one may easily obtain a pure glycerin. With a view to ascertain whether there are in commerce samples of glycerin absolutely free from arsenic—for in many works several processes are simultaneously used, and the glycerin will be mixed in the end—I examined ten samples of glycerin coming from ten different works. As I wished to detect smallest traces, I used silver nitrate instead of mercuric bichloride. Three of the samples would have to be rejected, four samples contained very small traces, which might be disregarded, while three only were absolutely free from arsenic.

There is still another process for saponifying fats, and consequently manufacturing glycerin, practised on a very large scale indeed, that which yields the soap-lye glycerin. At last year's Conference the glycerin derived from that source was very badly treated, and it was demanded that soap-lye glycerin ought to be entirely excluded from pharmacy. Unnecessary precaution!—up to now, at least; for no chemically pure glycerin has been prepared hitherto from soap lees, owing to the difficulties incident to the purification of it.

Being wishful to prove here that soap-lye glycerin has a far worse reputation than it—or, let me say, some of it deserves, I undertook during the last few weeks to prepare chemically pure glycerin from soap-lees, not in the laboratory, but on a large scale, in the works. I had to use such glycerin as I just had at hand, and as this contained, owing to the impure reagents, some arsenic, I had on starting to expect a glycerin containing traces of arsenic; but this is, from reasons pointed out above, only of secondary importance, as on repeating the manufacture of it, I shall have to start with purer reagents, and the real difficulties are lying in quite another direction.

Arsenic, although the most objectionable impurity, is, however, not the only one which may be found in "chemically pure" glycerin. As the British Pharmacopœia treats glycerin somewhat cursorily, I may be allowed to point out here one or two tests which will perhaps be found useful.

The glycerin may contain organic impurities, either fatty acids, &c., or so-called polyglycerols, under which name I may summarise all those substances having a higher boiling point than glycerin itself. The way to test for the latter is to gently evaporate a known quantity of glycerin in a platinum dish at a temperature of 160° C. The residue left, from which the ash, subsequently found on incineration, has to be deducted, will give a fair indication as to the care with which the glycerin has been distilled.

The following table gives the residues for eight "chemically pure" glycerins, arranged according to the quantity of organic residue, to which I have added the analysis of the soap-lye glycerin :—

| | Organic residue. Per cent. | Ash. Per cent. |
|---|---|---|
| 1 .. .. .. .. | 0·0243 | 0·00603 |
| 2 .. .. .. .. | 0·0327 | 0·0050 |
| 3 (*a*) .. .. .. | 0·0328 | 0·0140 |
| (*b*) .. .. .. | 0·0267 | 0·0102 |
| 4 .. .. .. .. | 0·0360 | 0·0138 |
| 5 .. .. .. .. | 0·0371 | 0·0081 |
| 6 .. .. .. .. | 0·0443 | 0·0066 |
| 7 .. .. .. .. | 0·0738 | 0·014 |
| 8 .. .. .. .. | 0·0751 | 0·0154 |
| 9 .. .. .. .. | 0·0931 | 0·0305 |

No. 3 represents the figures found for two batches of the soap-lye glycerin, which I have shown.

Fatty acids, as butyric acid, &c., and other organic impurities will be easily detected by testing with ammoniacal silver nitrate at ordinary temperature, which is recommended by the German Pharmacopœia. It is required of a good glycerin that it should not reduce the silver within fifteen minutes. This test is far more delicate than that in which silver nitrate alone is used, as the manufacturers of cosmetics do, who reject any glycerin which reduces silver nitrate in less than twenty-four hours. I think that the test with ammoniacal silver nitrate is a little too rigorous, as ammoniacal silver nitrate is easily reduced by glycerin at an elevated temperature; in fact, of all the glycerin samples I examined, there were only two (Continental ones) which fairly responded to this test, while all others would have to be rejected. Testing with nitrate of silver alone would perhaps be sufficient to show whether there are any silver nitrate-reducing substances in the glycerin.

Under No. 68 of the blue list an answer is requested to the question how to estimate glycerol in pharmaceutical preparations. I am afraid there is no satisfactory answer to that question, as we are not yet in possession of sufficient quantitative material. Lately, two methods have been proposed for the estimation of glycerol, which seem specially suitable in a great many cases, unhappily not in all. The first method, based on oxidation of glycerol to oxalic acid, can only be of use where no other organic substance is present which might yield oxalic acid. The glycerol in glycerinum aluminis might be thus estimated. The second method—boiling of glycerol with acetic anhydride and sodium acetate—requires highly concentrated solutions, and would, of course, be completely useless when other substances are present which combine with acetic anhydride, as would be the case with *e.g.*, glycerinum acidi carbolici, or glycerinum acidi gallici and glycerinum acidi tannici. For such preparations it would be required to have a method for completely transforming the glycerol into a weighable substance, *e.g.*, a tribromine derivative.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*Ordinary Meeting, January 13th, 1893.*

Prof. G. F. **Fitrgerald**, M.A., F.R.S., President, in the Chair.

Mr. **Hazelfoot** was elected a member of the Society.

Mr. F. W. **Sanderson**, M.A., read a paper on "*Science Teaching.*"

In this communication the author considers the methods of teaching physical science, and remarks that other sciences may best be treated in some different manner.

The method recommended is one found suitable in public schools where boys may remain till about the age of nineteen. In elementary and secondary schools modification would be necessary with a view to making it more immediately useful, whilst in university and technical colleges other methods might be preferable. The object of his public school method was to make physical science a definite means of education, rather than to produce skilled physicists. Certain mathematical subjects, such as arithmetic, geometry, and algebra, should be taught before physics is begun, and taught in such a way as to aid subsequent physical work.

In teaching arithmetic it is deemed advisable to distinguish between the science and the art of it, and to have separate hours for instruction in each. The subjects included in each part are described in some detail in the paper. No existing arithmetic satisfies the author's requirements.

Geometry is considered of the first importance; practical geometry and the use of instruments forming the best introduction to the subject. It is recommended that the elementary part be taught by the mathematical master, with a view to formal geometry, *e.g.*, Euclid. As most practical geometries consist of isolated constructions, they are useless for teaching the subject in a scientific manner. A number of problems suitable for a graduated introductory course are given.

After elementary geometry, mensuration may be taken up with advantage, the facts being verified by drawing to scale, measuring, or by weighing, but no rules being given.

Trigonometry of one angle may then be commenced. Here also free use should be made of the drawing-board, each pupil finding the sines, cosines, and tangents of angles by drawing and measurement, and making tables.

Quite independent of the mathematical class, the author has been in the habit of carrying boys on the engineering side through a course of graphical analytical geometry, in which they draw straight lines and the quadratic curves, &c., from their equations, solve simultaneous linear equations, quadratics, cubics, &c. Other geometrical constructions follow.

The subject as to what branches of science should be taught in the different departments of a school is then considered, and schemes are given for the classical, modern and commercial, science, and engineering sides.

Some general principles which have been kept in view in arranging the physical teaching are next described. In the first place, the fundamental experiments and observations on which each scientific law is based are explained to the pupils, and when possible the experiments are performed by the boys in the laboratory. Secondly, from the experiments the laws are stated as precisely as possible, the form of statement depending on the knowledge possessed by the class. The problem of expressing a law mathematically from its most fundamental statement is then fully considered. Thirdly, mathematical deductions from the laws are followed out, and the pupils perform experiments to verify results, and thus confirm the laws. Fourthly, a course of exact physical measurements is given, which includes mensuration, hydrostatics, mechanics, sound, heat, electricity, and light.

A first and second year's course is arranged in each subject, and in both years all the boys work the same experiment at the same time. This necessitates multiplication of apparatus, but being of a simple character in the lower forms, where the pupils are numerous, it is not prohibitive. It is also stated that boys get better results with comparatively rough apparatus, if large, than with delicate and expensive instruments. About half the time devoted to physics is spent in the laboratory.

Mathematics is introduced as far as can be done without straining the pupils too much, and with young classes appeal is made to experiment where the strictly logical argument would be difficult to follow.

Instead of teaching the applications of science as done in some technical schools, the author's method is to teach pure science, and let the applications come in as illustrations.

At the end of the paper detailed lists of experiments for practical courses in electricity and optics are given. Samples of the apparatus used were exhibited at the meeting, those for optics being particularly simple and ingenious.

Prof. A. M. Worthington said his experience led him to a very hearty agreement with Mr. Sanderson on all essential points, and he thought there was now a close agreement amongst teachers as to the best methods. He therefore wished to ask: Had not the time now come at which the Physical Society might usefully endeavour to exert direct influence on science teaching? As the scientific instruction of a person who intends following a scientific calling is generally divided into stages and conducted in different places under different teachers, he thought it was desirable that those in charge of his training at each stage should say up to what point his instruction should be carried before he reaches them.

Other matters in which the Society might do useful work were, first, reporting on text-books and condemning the bad ones, and, second, furthering the adoption of the decimal system.

At present, he said, an enormous extension in the teaching of physical science is taking place, and it seemed within the power of the Physical Society to place itself at the head of the movement. Another point which required to be settled was the relative importance of physics and chemistry at different stages of a student's education.

Mr. L. Cumming agreed with the general principles laid down by Mr. Sanderson. In attempting to carry out such schemes numerous difficulties presented themselves, especially where the science master had not control over the subdivision of the boys' time. He had tried teaching the science of arithmetic to boys in the lower forms, but the results were not encouraging, for he found very few who could do much in it. They seemed to devote themselves much more readily to concrete problems and the art of manipulation of rules. Graphical statics was very valuable. As regards experimetal lectures, he believed them to be very important, especially in junior classes. For scholarship boys a different method had been tried with success. Instead of performing lengthy experiments completely before the class, the essential parts were gone over, and for the minor points the results obtained in experiments made before or after the lecture were given, so that all the data for reducing the results were to hand. This saved considerable time. He had hoped Mr. Sanderson would say something about the slide rules, and wished to learn his opinions on its use.

Dr. Stoney said he was very much struck with the methods of teaching brought forward by Mr. Sanderson, and remarked that his own work would have been considerably lightened if such a scheme had been developed many years ago. Experimental methods were very valuable, provided the inaccuracies of measurement be kept in view. Plotting curves was also very instructive, and might be made a means of furnishing the fundamental notions in the differential and integral calculus. As to the introduction of chemistry, his experience went to show that this should be done at an early age. Dynamics should also be begun early.

Mr. W. B. Croft thought that if the Society did make rules to regulate the teaching of physical science, these rules should not be too strict, for the ages and aims of boys might differ widely. At Winchester the science teaching was carried out on the lines recommended by a committee of the Royal Society appointed to consider the subject. (Leaflets showing the scheme adopted were here distributed to members.) The object of the scheme was not merely to make science a means of education, but an integral part of the education of his pupils. He also made a point of keeping the lecture experiments up to date.

Mr. Rentoul said dynamics should not be taught as a mathematical subject, but experimentally. He thought it of the first importance that boys should learn how to find out facts for themselves, and for this practical work was essential.

Prof. Ayrton remarked that the conditions under which science was taught differed in different places. He himself taught with the object of enabling the persons under instruction to improve the industry. For this purpose he believed the analytical method more suitable than the synthetical one adopted by Mr. Sanderson. It also had the advantage of being more scientific, for it was more natural, being, in fact, that used by children from birth, for they had no other means of learning the nature and properties of their surroundings. In his first year's technical course the work was synthetical, whilst in the third year, the students having analysed existing apparatus, were taught to devise new or improved forms, and hence the work became more synthetical.

Mr. F. J. Smith said it was important that students be taught to measure by the balance, micrometer, spherometer, &c., as soon as possible. He also inquired how far Mr. Sanderson's pupils could help themselves in making the apparatus required for the simple experiments.

Dr. Gladstone agreed with many points in the paper. Lately he had had to do with schemes for improving the teaching in elementary schools. Children were naturally philosophers, but at present their curiosity was considered objectionable and sternly repressed. Efforts were now being made to alter this state of things. Kindergarten classes in infant schools were a step in the right direction. It was very difficult to introduce analogous methods in the higher standards, but natural science had now obtained a footing. Although the methods of teaching adopted might be those suitable for pure science, care should be taken to put in practical illustrations, for when suitably chosen, they are sources of great interest to children.

Mr. Sanderson, in reply, said the slide rule was used throughout the course. Mechanics was taught by actual machines, such as pulley blocks, screw jacks, &c. The boys made some apparatus, but to make all would require too much time.

The President, when proposing a vote of thanks to the author of the paper, said that in Ireland the opinion that boys and girls cannot be taught science greatly predominated. They found considerable difficulty in getting any continuation of the kindergarten teaching sanctioned. Possibly drawing might be allowed, but this seemed all they could hope for at present. He wished to emphasise the fact that in such schools the object was education, and practical applications of science were not important except in so far as they created an interest in the subjects. At present scientific teaching was in an experimental stage, and as in other things, progress is made by trial and error. Many different methods were being tried, and it was important to know which were successful and which failures. He thought the Physical Society might be useful in collecting information on the subject by issuing a circular of questions to science teachers, and subsequently drawing up a report on the subject.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 2, January 9, 1893.

**The Drainage Waters of Cultivated Land.**—P. P. Dehérain.—The drainage of cultivated soils is much less abundant than that of bare soils, and it is the less the longer the ground is occupied. In agriculture the object to be aimed at is to cover the soil with a plant sufficiently luxuriant in its vegetation to evaporate all the rain-fall. The loss of nitrogen compounds is regulated not by the composition of the drainage, but by its abundance. All the nitrogen nitrified in the soil is either assimilated or lost. Thus, when the crop is small the farmer is doubly injured: by the deficiency of the products obtained and by the impoverishment of his land.

**The Purification of Arsenical Zinc.**—H. Lescoeur.—Zinc intended for toxicological operations may be obained by a double treatment: an oxidation with nitre and a fusion with zinc chloride. The metal thus prepared is totally free from arsenic, antimony, sulphur, and phosphorus. It contains iron, lead, copper, &c. But the presence of these metals occasions no inconvenience.

**Combinations of Quinoleine with the Haloid Salts of Silver.**—Raoul Varet.—Quinoleine in excess, acting upon silver chloride, bromide, and iodide, yields compounds containing 1 mol. of base to 1 mol. of salt. These compounds are more stable than those obtained with pyridine, probably because the vapour tension of pyridine at the ordinary temperature is considerable. The compounds produced by pyridine and quinoleine, tertiary bases, are less stable than those formed by piperidine, a secondary base. Silver chloride, bromide, and iodide do not dissolve in quinoleine, contrary to what takes place in pyridine and piperidine. This fact is probably due to the presence of the benzenic nucleus in quinoleine. Silver cyanide dissolves very easily in quinoleine, forming a compound containing 2 mols. base to 1 mol. of salt. It is of the same type as that produced by piperidine.

**Symmetric Propylurea and Dipropylurea.**—F. Chancel.—The author prepares the former substance by the action of propylisocyanate upon aqueous monopropylamine. It melts at 104°, and boils at 255°. It is sparingly soluble in cold water; rather more readily in hot water. Its best solvents are alcohol and especially ether. Dipropylsulphurea melts at 68°.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxi., Part 5.

**Determination of Clay and Sand in Soils.**—Dr. F. Tschaplowitz.—In the sense of agricultural and horticultural practice, we may regard as clay all those constituents of the soil free from humus and carbonate which are insoluble in dilute hydrochloric acid and in alkali. It appears that elutriations can be effected with the same certainty in a precipitation cylinder as in Schöne's apparatus. Clay may be opened up by prolonged boiling in a Kjeldahl flask. All equally insoluble material free from humus and carbonate, but of higher hydraulic value than from 0·01 to 0·0006 m.m., is to be regarded as sand.

**Analysis of the Nitrogenous Constituents present in Commercial Peptones.**—A. Stutzer (of Bonn).—This paper will be inserted if possible.

**Determination of Phosphoric Acid in Basic Slags.**—Dr. A. F. Jolles (of Vienna).—Already inserted.

**Method of Determining Thallium by Titration.**—K. Sponholz.—This paper will be inserted in full.

**Precipitation of Alumina in Presence of Salts of Lithium.**—K. and E. Sponholz.—To be inserted in full.

**Proportion of Fluorine in Bones and Teeth.**—Dr. S. Gabriel.—This memoir will be inserted in full.

**Contributions to Kjeldahl's Process for the Determination of Nitrogen.**—Carl Arnold and Konrad Wedemeyer.—(See p. 37).

**Analysis of Lard.**—C. Amthor and Julius Zinc.—The authors recommend the use of the solution as originally prescribed by Von Hübl.

**Quantitative Determination of Antimony and the Gooch Crucible.**—Th. Paul.—This paper requires the accompanying illustration.

**A Continuous Gas-generating Apparatus.**—Alex. von Kalecsinsky.—This paper also requires the illustration appended.

**Spectra of Copper, Silver, and Gold.**—H. Kayser and C. Runge.—From the *Annalen Physik Chemie.* No particulars are given.

**Position of Absorption-Bands, and the Sensitiveness of Organic Colouring-Matters to Light.**—E. Vogel (*Annalen Physik Chemie*).—No details are given.

**Action of Sulphuric Acid, Dilute or Concentrated, upon Potassium and Sodium Bromides and upon Hydrobromic Acid.**—Frank T. Addyman.—(From the *Jour. Chem. Soc.*).

**Action of Dilute Sulphuric Acid upon Zinc.**—Frank Pullinger.—(From the *Jour. Chem. Soc.*).

**The Use of Platinum Resistance Thermometers.**—H. L. Callendar and E. H. Griffiths.—(From the Chemical News).

**Researches on the Action of Different Metals, Metallic Salts, Acids, and Oxidising Agents upon Caoutchouc.**—W. Thomson and F. Lewis.—(From the Chemical News).

**Determination of Melting-Points.**—Arnold Reissert (*Ber. Deut. Chem. Gesell.*).—The author has submitted the various methods of determining melting-points to a careful examination, and, like Landolt, comes to the conclusion that not only the various methods of determination yield discrepant values, but even determinations effected on one and the same method do not entirely coincide. The values obtained by the application of capillary tubes are generally too high, especially if the temperature is raised too quickly and the point of complete fusion is observed. The apparatus with a ball signal also gives too high results, and the higher the more rapidly the temperature rises. The method recommended by Landolt as the most accurate requires at least 20 grms. of substance, and is therefore in most cases inapplicable, so that the use of capillary tubes must be retained in practice. To obtain the most accurate results possible, the author recommends the following precautions. 1. The zero-point of the thermometer, used for the determinations, must be determined from time to time, and the corresponding correction must be made. 2. The correction for the projecting mercurial filament must always be made, as without it differences of several degrees may be produced in consequence of the different error. The excellent tables worked out by Reinbach greatly simplify the application of this correction. 3. The point of incipient melting should always be taken (in pure substances only!), as the temperature in the interior of the capillary tube is always rather higher than at the sides. An apparatus with an electric signal-bell has been designed by A. C. Christomanos.

**Acceleration of Evaporation in Small Vessels.**—E. Whitfield.—(From the *Journal of Analytical and Applied Chemistry*).

**New Nitrometer for Determining Nitrogen in the Salts of Ammonium.**—W. Hentschel (*Berichte Deut. Chem. Gesell.*).—A description of this apparatus is of little use unless illustrated. According to the inventor, no corrections are necessary except the utmost accuracy is required, since the absorption of the nitrogen in the hot liquid is essentially less than in such of ordinary temperature.

## MEETINGS FOR THE WEEK.

Monday, 30th.—Medical, 8.30.
—— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Gurrents," by Prof. J. A Fleming, F.R.S. (Cantor Lectures).
Tuesday, 31st.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
Wednesday, Feb. 1st.—Society of Arts, 8. "The Purification of the Air Supply th Public Buildings and Dwellings," by William Key.
Thursday, 2nd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical Society, 8. "The Connection between the Atomic Weight of the Contained Metals and the Magnitude of the Angles of Crystals of Isomorphous Series," by A. E. Tutton. "Note on Optical Properties other than Colour as indicative of Structure." by Prof. H. E. Armstrong. "Contribution to the Knowledge of the Aconite Alkaloids. IV. Napelline," by Prof. W. R. Dunstan and E. T. Harrison.
—— Royal Institution, 3. "Tennyson," by the Rev. Canon Ainger, M.A., LL.D.
Friday, 3rd.—Royal Institution, 9. "Theory and Practice in Electrical Science," by Alexander Siemens, M.Inst.C.E.
—— Geologists' Association, 7.30. (Anniversary).
—— Quekett Club, 8.
—— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
Saturday, 4th.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

## TO CORRESPONDENTS.

*E. Woodhead.*—No method is known by which the yellow modification of iodide of mercury can be rendered permanent so as not to change easily into the red iodide.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1732.

## KOENE AND STAS:

### Chemistry at Brussels in 1840—1860.

By Dr. T. L. PHIPSON, F.C.S.;
Formerly of the University of Brussels; Member of the Chemical Society of Paris, &c.

Shortly after the Revolution of September, 1830, which resulted in the division of the Netherlands into two independent kingdoms, the people of Brussels deemed it necessary to found a University. So, one fine day, a number of good citizens, headed by the Burgomaster, proceeded to the Hotel de Ville, and, after listening to a magnificent piece of music performed by the orchestra of the Royal Harmonic Society, delivered some enthusiastic speeches, and the University of Brussels was duly called into existence with all proper forms and ceremonies (Oct. 20, 1834).

Fifteen years later, I became enrolled as a student in that University, where I passed some of the happiest years of my life. After a long course of Philosophy, I entered the faculties of Science and Medicine, devoting particular attention to chemistry under Prof. C. J. Koene, the rival of Stas. The latter was Professor of Chemistry at the Ecole Militaire, and Melsens, another well-known chemist, lectured at the Ecole Vétérinaire.

Koene was a disciple of Berzelius, he was a Doctor of Science, and had gained his professorship by dint of hard work and indomitable application; he enjoyed no patronage whatever. Berzelius himself had translated into Swedish Koene's paper on "Aqua Regia," and inserted it in the *Transactions* of the Academy of Stockholm.

Stas, like the worthy chemist Melsens, was highly recommended as the pupil and friend of Jean Baptiste Dumas, with whom they had both worked in Paris, and to whose powerful patronage Stas owed everything. I am not aware that he ever graduated in any University, but after having obtained the Professorship of Chemistry at the Ecole Militaire, he succeeded in getting himself elected into the Belgian Academy of Sciences, and, many years later, as a Corresponding Member of the Paris Academy. As an old pupil and *collaborateur* of Dumas, he, of course, brought foward the new theories of the latter, which were combatted by Berzelius and by Koene, but he had no great field for developing them; young soldiers, as a rule, make poor chemists.

At the University, where the doctrines of Berzelius, Mulder, and Liebig were professed in the most able manner by Dr. Koene, the new ideas in organic chemistry then cropping up were rather rather severely criticised, if not ridiculed, and it was plainly predicted that should they gain ground, they would lead organic chemistry into a state of chaos. Some of my friends are inclined to think that this prediction has been tolerably well realised.

What first brought Stas into notice in Brussels was the celebrated "Affaire Bocarmé," in which a certain Count Bocarmé had poisoned his brother-in-law by means of nicotine, which he obtained by distilling tobacco leaf. In these operations, it was said, his victim occasionally assisted him. Koene was (or pretended to be) much hurt that the Government called upon Stas, who was only Professor of the Ecole Militaire, to make the chemical investigations in this case, which should have been given to the Professor at the University. Stas found nicotine in the body, but only—as Dr. Koene took care to remind his pupils—after he had found two bottles of it in a cupboard. Anyhow, this affair led Stas, after the execution of Count Bocarmé, to the publication of an important paper on the isolation of alkaloids in cases of poisoning, which has proved of considerable value to science.

Koene was a very expert chemist and an excellent professor.* In his lectures he rarely referred to notes. There were a few specimens and flasks on the table before him, and a large black board behind him, to which he turned now and then and covered it with formulæ. To his left stood the docile laboratory assistant, a dull timid individual, who once allowed the air to get into a large jar of phosphuretted hydrogen as he carried it from the laboratory to the adjacent lecture room, making his entry with a flame which rose to the ceiling; and on the right of the professor was a large Dutch stove, which in winter proved a great comfort, as the lectures began at eight in the morning.

He had also a course of toxicology in the afternoon at three o'clock, twice a week. Besides his professorship at the University, Koene held the appointment of superintendent or consulting chemist to the Mint, and to the large chemical works of Van der Elst,† and was occasionally engaged on Government Commissions. On such occasions he was frequently thwarted by Stas; for between these two professors there existed very great jealousy. It was an open secret that Stas envied Koene his chair of chemistry at the University; whilst Koene was no less vexed at seeing Stas elected a member of the Belgian Academy of Sciences, and used to speak of him sarcastically as "*the savant*," &c. Although a man of kindly disposition, and a warm-hearted friend, Koene's excessive pride and violent temper, no less than his comparatively short life, strongly militated against his successful competition with a cool-headed man of the world like Stas, who has outlived him by about thirty years. Nevertheless, the "Mémoires de Chimie" which Koene has left in one small volume form a lasting monument ot ingenious, indefatigable study, and may have their influence on the progress of chemical thought when some of our modern theories are abandoned. He has, among other things, the merit of having reformed our ideas of *neutrality*, and his views were soon universally adopted.

When we compare the work of Koene with that of Stas, it is easy to see that the former possessed the more expansive mind. While Stas limited himself to a small point of philosophy, and to a few purely analytical problems, Koene in his lectures and writings covered a much larger field of thought. We may admire Stas as a laborious painstaking specialist, not without a certain amount of genius; but Koene was possessed of far greater originality of views, and of an impetuous character, which, combined with an ardent love of truth, caused him to grapple with many of the greater phenomena of Nature.

Koene was the first who made use in his lectures of the pure nomenclature of Berzelius; whilst the French professors and their followers used such terms, for instance, as "sulphate of protoxide of iron," "sulphate of peroxide of iron," Koene invariably said "ferrous sulphate," "ferric sulphate," and so on, throughout the whole of inorganic and organic chemistry, just as we have lately begun to do in England. In organic chemistry the *compound radical* theory was used with rare talent. The *equivalent notation* and *dualistic* system (devoid of all hypothesis) were alone used, and in the entire course of the lectures nothing was stated that could not be verified by actual experiment. For instance, MO,HO was not allowed to be $MO_2H$, since HO could be separated by the mere action of a slight heat, and the supposed body $MO_2$ could not be isolated, whilst MO could be, and was known to exist, &c.

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* He was a powerfully built man, of medium height; black hair, eyes, and beard; and swarthy complexion; with a Roman nose, and decided Jewish aspect; always extremely plain and neat in his attire; he usually wore black silk gloves when walking. His manners were polished and modest, unless when irritated, then his dark gypsy-like eyes would flash fire, and his amiable qualities disappeared.

† Pierre Van der Elst, the founder of these works, was the first to erect leaden chambers for sulphuric acid—this was in the year 1763.

In 1856 was published the first part of Koene's "Mémoires de Chimie" ("Mémoires de Chimie," par le Dr. C. J. Koene, Professeur de Chimie et de Toxicologie à l'Université de Bruxelles. Première Partie. Bruxelles: P. Larcier, Libraire de l'Université, 1856). This little volume comprises papers reprinted from the *Bulletin de l'Académie des Sciences*, of Brussels, *Poggendorff's Annalen*, and the *Annales of the Academy of Sciences* of Stockholm. Others which have appeared in the *Annales de Chimie et de Physique*, and in certain periodicals devoted to agriculture, were, unfortunately, never collected. At the same time, he published a volume of "Popular Lectures," consisting of four public lectures delivered in the Academical Hall of the University and reproduced by A. Tardieu, stenographer to the Legislative Assembly. It is there he discusses the probable constitution of the atmosphere from remote geological ages to the present time, criticising the views of Berzelius, Mulder, Dumas, and Liebig on this interesting subject; and there is also a very severe criticism of a report by Stas on the acid emanations from the chimneys of the Mint, which, I remember, caused great laughter among the crowded audience.

Koene's paper on the neutrality of salts, published in 1842, is a marvel of chemical reasoning, and had great effect on the science of his day; and the same may perhaps be said of his paper on "Aqua Regia," his "Lessons on the Constitution of Salts," and several others.

Stas had, no doubt, enjoyed a far better laboratory training than Koene. Clever and painstaking analyst as the latter may have been for that period, he had not had the advantage of working with Dumas in Paris, and the Belgian Government knew what it was about in confiding to Stas, instead of to Koene, the toxicological investigations in the Bocarmé case. With regard to the extreme care taken by Stas in his investigations on *acetal*, on the *amniotic fluid* of the fowl, and on the *atomic weights* of certain elements with the view of deciding for or against the law of Prout, &c., no doubt the greatest accuracy that could be obtained in the laboratory is made manifest. Nevertheless, Prof. Hinrichs has lately shown (*Comptes Rendus*, Dec., 1892) that the oxygen figure in Stas's determinations with potassic chlorate, increases with the quantity of salt taken for analysis by the dry method, and decreases with the quantity taken when the wet method is used; reminding us, once more, that perfection is not attainable in this world.

It will be gleaned from these considerations that at Brussels, during the period of which I write, we had in Koene the last representative of the great schools of Berzelius and Liebig; and in the persons of Stas and Melsens the first representatives of the new French school. They were all highly meritorious chemists, but Melsens was perhaps the greater philosopher of the three, a man of an exceedingly amiable disposition, and universally beloved by his friends and pupils. Had Stas been at the University instead of the Ecole Militaire he might have drawn around him young men devoted to science. Koene's classes, like those at Edinburgh at the present day, were filled almost entirely by medical students. The University in Brussels made few scientists, philosophers, or diplomatists. It was the resort of men destined to live by law or by medicine, and it was a matter of surprise and some talk in the Brussel's newspapers when my paper on "Catalytic Force" took the gold medal in the public competition of the Société Hollandaise des Sciences at Haarlem (1857). Koene was more proud of this than if he had written the paper himself, and took care to remark that no pupil of Stas had ever done such a thing.

Poor Koene was dead when another gold medal fell to my lot in 1868 from the Royal Society of Medical and Natural Sciences of Brussels. His successor, Jean Baptiste Francqui, obtained his doctor's degree six months later than I did; he was elected professor when I had already left Brussels for Paris. Francqui was one of Koene's favourite pupils and a scientific chemist of great promise, who, after visiting, at the request of the Belgian Government, the principal laboratories in Europe, superintended the re-construction of those at the University of Brussels. He unfortunately succumbed to illness very early in life. Most of Koene's other pupils were destined for pharmacy or medicine, and some of them have become very distinguished men in their respective professions. The pupils of Jean Servais Stas were drafted into the army on leaving the Ecole Militaire. As I have already stated, Stas has outlived Koene by about thirty years, during which time his reputation as a careful analyst and scientific chemist has become greater than it was at the time of the Bocarmé affair, which first brought him into notice.

I hope some day to examine Koene's theory of the constitution of the atmosphere, for which I have no space here. The foregoing remarks will, I trust, prove interesting at a time when the career of Stas is attracting so much attention at the Chemical Society.

Putney, Jan. 27, 1893.

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## ON POISONING BY TINNED BEEF.

By THOMAS K. LEWIS.

Twenty cases of poisoning resulted from eating canned corn beef, sold October, 1892. The symptoms of poisoning were noticed in from two to five hours after eating.

Eighteen hours after the meat was sold a preliminary examination was made for lead and tin. The physicians attending the persons stated that they thought that the poisoning was due to inorganic poisons coming from the action of the meat on the can.

About 50 grms. of the meat was burned to a light ash, and tested for tin and lead. Nothing but a small quantity of iron in harmless quantities was found, and which is found in all meat.

Ptomaïnes were suspected, and then a systematic examination was made for them.

An alcoholic extract was made. The meat was minced finely and well shaken with an equal weight of absolute alcohol for some time, the meat and alcohol being heated to 75° C. The alcohol was filtered away and evaporated by means of a water-bath and air-pumps. The bath was not allowed to reach a temperature higher than 75° C. The solution by this means only reached 40°—45° C. Evaporation continued until a thick extract remained containing some fat, which was dissolved by the alcohol in the extraction from the meat. This fat, which was now precipitated, was filtered away from the extract, which was diluted with a small quantity of absolute alcohol, and evaporated again. A reddish yellow liquid resulted, which had a very sickening odour.

Tests were made as follows:—From an ethereal extract potassium ferricyanide and ferric chloride were mixed, and a few drops of the extract added, which produced a deep blue colour in a few minutes. This showed a reduction of the ferri- to the ferro-cyanide of iron, which is the most satisfactory test we have for ptomaïnes.

Another test:—A solution 1 to 10 of ether was made of the extract, and a few drops of strong $H_2SO_4$ was added. A yellow and then a rose-red colour was noticed, also a very prominent odour of amines.

After eighteen days the same methods were employed without success, for no tests could be obtained.

When the meat was first analysed it was used to experiment on animals. It was found to be poisonous to them. Eighteen days after the poison was discovered the meat was again fed to some animals; no symptoms of poisoning occurred.

From the foregoing data, after having consulted "Blythe on Poisons" and "Prescott's Organic Analysis," and several minor works, the following was decided:—

That there were no inorganic poisons, lead or tin, present in the meat, because they were not found by testing, and because no poison was found in the meat at the close of the work.

The poison must have been decomposed, a thing which could not have occurred had it been inorganic poisoning. Hence ptomaïnes were indicated both by tests and by the poison having decomposed.

Further, a ptomaïne called neuridine has been recorded, which decomposes a short time after it has been formed. Therefore we would state that the poison was a ptomaïne, and would identify it as neuridine.

Ohio State University, Columbus, Ohio,
January 9, 1893.

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## A NOTE ON THE METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By PHILIP E. BROWNING.

Recent work on my method for the quantitative separation of strontium from calcinm by the action of amyl alcohol on the nitrates (*American Journal of Science*, vol. xliv., December, 1892) has demonstrated the possibility of using very much smaller amounts of amyl alcohol in the boiling than the amounts formerly used (30 c.m.$^3$ for each treatment). By the use of smaller beakers (50 c.m.$^3$ capacity), 10 c.m.$^3$ of the alcohol can be conveniently substituted for 30 c.m.$^3$, and the correction for solubility of the strontium nitrate is thus reduced from 0·001 grm. on the oxide to 0·0003 grm. in each treatment, and the corresponding amount of sulphate to be abstracted from the calcium sulphate before calculating to the condition of oxide is reduced from 0·0017 grm. to 0·0005 grm. in each treatment. The necessity of a double treatment, or the use of two portions of 10 c.m.$^3$ each of the alcohol, brings the total correction to 0·0006 grm. on the strontium oxide, and 0·0010 on the calcium as sulphate. For ordinary work such a correction may be disregarded. The following Tables give the corrected and uncorrected results.

Table I. (Correction Disregarded).

| | SrO taken. | SrO found. | Error. | CaO taken. | CaO found. | Error. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| 1. | 0·0570 | 0·0565 | 0·0005 − | 0·0534 | 0·0540 | 0·0006 + |
| 2. | 0·0573 | 0·0567 | 0·0006 − | 0·0534 | 0·0543 | 0·0009 + |
| 3. | 0·0285 | 0·0274 | 0·0011 − | 0·0272 | 0·0276 | 0·0004 + |
| 4. | 0·0568 | 0·0560 | 0·0008 − | 0·0535 | 0·0537 | 0·0002 + |
| 5. | 0·0568 | 0·0561 | 0·0007 − | 0·0533 | 0·0535 | 0·0002 + |
| 6. | 0·0288 | 0·0280 | 0·0008 − | 0·0271 | 0·0272 | 0·0001 + |
| 7. | 0·1420 | 0·1416 | 0·0004 − | 0·0535 | 0·0544 | 0·0009 + |
| 8. | 0·1419 | 0·1416 | 0·0003 − | 0·0665 | 0·0669 | 0·0004 + |
| 9. | 0·1135 | 0·1132 | 0·0003 − | 0·1066 | 0·1070 | 0·0004 + |
| 10. | 0·1137 | 0·1126 | 0·0011 − | 0·1064 | 0·1070 | 0·0006 + |

Table II. (Correction Applied).

| | SrO taken. | SrO found. (Correc.) | Error. | CaO taken. | CaO found. (Correc.) | Error. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| 1. | 0·0570 | 0·0571 | 0·0001 + | 0·0534 | 0·0536 | 0·0002 + |
| 2. | 0·0573 | 0·0573 | 0·0000 | 0·0534 | 0·0539 | 0·0005 + |
| 3. | 0·0285 | 0·0280 | 0·0005 − | 0·0272 | 0·0272 | 0·0000 |
| 4. | 0·0568 | 0·0566 | 0·0002 − | 0·0535 | 0·0533 | 0·0002 − |
| 5. | 0·0568 | 0·0567 | 0·0001 − | 0·0533 | 0·0531 | 0·0002 − |
| 6. | 0·0288 | 0·0286 | 0·0002 − | 0·0271 | 0·0268 | 0·0003 − |
| 7. | 0·1420 | 0·1422 | 0·0002 + | 0·0535 | 0·0540 | 0·0005 + |
| 8. | 0·1419 | 0·1422 | 0·0003 + | 0·0665 | 0·0665 | 0·0000 |
| 9. | 0·1135 | 0·1138 | 0·0003 + | 0·1066 | 0·1066 | 0·0000 |
| 10. | 0·1137 | 0·1132 | 0·0005 − | 0·1064 | 0·1066 | 0·0002 + |

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## A PLATINIFEROUS NICKEL ORE FROM CANADA.

By F. W. CLARKE and CHARLES CATLETT.

During the autumn of 1888 we received, through two different channels, samples of nickel ores taken from the mines of the Canadian Copper Company, at Sudbury, Ontario. From one source we obtained two masses of sulphides, to be examined for nickel and copper; from the other source came similar sulphides, together with a series of soil and gravel-like material, seven samples in all. In the latter case an examination for platinum was requested, and in five of the samples it was found, the gravel above mentioned yielding 74·85 ounces of metals of the platinum group to the ton of 2000 pounds. At the outset of the investigation we were decidedly incredulous as to the existence of platinum in such ores; but the discovery of sperrylite by Mr. Wells in material from the same mines gave our work a wholesome stimulus, and the assays were carefully carried through.

The sulphide ores submitted to us from Sudbury were all of similar character. They consisted of mixed masses, in which a grey readily tarnishing substance was predominant, with some chalcopyrite, possibly some pyrite, and a very little quartz. Two samples were examined in mass; one gave 31·41 per cent of nickel with a little copper, the other gave 35·39 per cent of nickel and 5·20 of copper. The nickel mineral itself proved to be a sulphide of nickel and iron, and as ores of that composition are not common, it was thought desirable to examine the substance further.

As above stated, the nickel mineral is the predominating constituent of the masses submitted for examination. It is steel grey, massive, and exceedingly alterable in the air, and its specific gravity, determined by pycnometer, is 4·541. An analysis of carefully selected material gave the following results:—

| | |
|---|---|
| Ni .. .. .. .. | 41·96 |
| Fe .. .. .. .. | 15·57 |
| $SiO_2$ .. .. .. | 1·02 |
| Cu .. .. .. .. | 0·62 |
| S .. .. .. .. | 40·80 |
| | 99·97 |

Neither cobalt nor arsenic could be detected.

The foregoing figures work out sharply into the ratio R : S :: 4 : 5; and approximately into the formula $Ni_3FeS_5$. If we deduct silica, together with the copper reckoned as admixed chalcopyrite, and re-calculate the remainder of the analysis to 100 per cent, we have the following figures:—

| | As found. | Calc. as $Ni_3FeS_5$. |
|---|---|---|
| Ni .. .. .. | 43·18 | 44·6 |
| Fe .. .. .. | 15·47 | 14·4 |
| S .. .. .. | 41·35 | 41·0 |
| | 100·00 | 100·0 |

In short, the mineral has the composition $Ni_4S_5$, with *about* one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. What relations it may bear toward beyrichite, pyrrhotite, &c., is as yet a matter of considerable uncertainty. Probably in most cases the nickeliferous constituent of pyrrhotite is millerite, but other sulphides, like the polydymite, may perhaps occur also.

The polydymite which was selected for the above analysis came from the mass in which, in average, 35·39 Ni and 5·20 Cu had previously been found. The mass weighed several kilogrms. and was remarkably free from quartz. The same mass, with two smaller pieces resembling it, were also examined for platinum, by the following

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* From the *American Journal of Science*, vol. xliv., December, 1892.—Contributions from the Kent Chemical Laboratory of Yale College.

method:—One assay ton of the finely ground ore was treated with nitric acid until all or practically all of the sulphides had been dissolved. The dried residue was then assayed in the usual manner; except that, to facilitate cupellation, a little pure silver was introduced into the lead button. From the final bead the silver was dissolved out by sulphuric acid, leaving the platinum in a finely divided grey powder. The latter dissolved easily in aqua regia, and gave all the reactions needful to identify it thoroughly. The results were as follows, "A" representing the large mass in which the polydymite was determined:—

| | Per cent. |
|---|---|
| A, 2·55 ounces Pt to the ton, or .. .. | 0·0087 |
| B, 1·8 ounces Pt to the ton, or .. .. | 0·0060 |
| C, 7 ounces Pt to the ton, or .. .. .. | 0·0240 |

That the metal weighed was nearly all platinum is certain; but it may have contained small amounts of other metals of the same group. The material separated was not sufficient to warrant a search for the rarer associates of platinum. Probably the platinum exists in the ore as sperrylite, although this point was not proved. The amount of platinum in the mass most thoroughly examined would require, to form sperrylite, only about 0·007 per cent of arsenic, which is too small a quantity for detection by ordinary analysis. That platinum should exist in appreciable quantities in an ore of such character is something quite extraordinary. Whether it could be profitably extracted is an open question.—*Bulletin of the United States Geological Survey*, No. 64.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending December 31st, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, January 10th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 173 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The condition of the water supply to the Metropolis during the month of December continued to be substantially the same as that prevailing during November, and commented on in our previous report. The proportion of organic matter present, as estimated alike by the oxygen and combustion processes, and by the degree of colour-tint of the water, was not excessive for the season of the year, and just a trifle lower than that present in the previous month's supply. In the case of the Thames-derived water, for instance, the mean proportion of organic carbon amounted to 0·192 part in 100,000 parts of the water, as against a mean of 0·202 part per 100,000 parts of water in the November supply, the maximum proportion found in any single example examined, or 0·286 part in 100,000 parts, being identical with the maximum met with in the November supply.

With two exceptions only, one recorded as "slightly turbid" and the other as "clear but dull," the whole of the 173 samples examined during the month were found to be clear, bright, and well filtered. In several instances no samples could be obtained from the standpipes during the last week of the month, by reason of the sharp frost then prevailing.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

ON THE

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

### *Preface.*

From his famous research on the composition of water (*Ann. Chim. Phys.*, Series 3, vol. viii., p. 189 *et seq.*) Dumas concluded that, in accordance with Prout's law, the "equivalent" of hydrogen, meaning the ratio $H_2:O$, is equal to one-eighth exactly, although the exact mean of his nineteen syntheses stood at 0·12515 (corresponding to H = 1·00120 for O = 16, or to O = 1598 for H = 1). Feeling convinced that his result was liable to a small negative correction, although he had already allowed for the adventitious water formed from the oxygen of the air which had been present in the dilute sulphuric acid which he used for the evolution of his hydrogen, and seeing that his individual results oscillated between 0·1247 and 0·1256, he had no hesitation in rounding off his mean and adopting 0·12500 as the nett result of his work. Strictly speaking, he had perhaps no right to make even this slight arbitrary correction, but his choice was confirmed very shortly after the publication of his memoir by an independent research of Erdmann and Marchand,† which, if it proves anything, shows that Dumas's adopted value is probably nearer the truth than his uncorrected mean.

With these two investigations before them, all chemists agreed in admitting that, however it may stand with Prout's law, the ratio O : H happens to be equal to sixteen exactly, and they continued doing so until Stas, in the course of his great research, came to determine the silver value of sal-ammoniac; and finding that the weight of sal-ammoniac, equivalent to Ag = 107·93, that is to say his "$NH_4Cl$," exceeded his sum N + Cl by more than four units, gave it as his conviction that the true ratio, O : H, cannot be greater than 15·96, corresponding to H = 1·0024 for O = 16. But Stas's own result is H = 1·0075, and this number, if it has any right to vote, is as incompatible with 1·0024 as it is with 1·0000. But Stas's guess was confirmed subsequently by Clarke, and, after him, again by Lothar Meyer and Seubert, who, in their respective recalculations of atomic weights, both arrived at precisely the same value. It is probably owing to this circumstance that the number 15·96 has been so generally adopted by chemists, and found its way into all the handbooks. All chemists, of course, have not adopted it in the same sense. With many, no doubt, it is no more than the arithmetically correct registration of what they take to be the most probable value for a strictly speaking unknown constant, which, for anything they can know, may perhaps lie closer to, say, 16·05 than to 15·96; but

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* *Proceedings of the Philosophical Society of Glasgow.*

† *Journ. Prakt. Chemie*, vol. xxvi., p. 461 *et seq.* Abstract in *Ann. Chim. Phys.*, immediately after Dumas's memoir.

not a few attach to it a higher significance, inasmuch as they take 15·96 to be the true value, and contrast it with the old 16 as with a mere approximation, just as one might contrast Berzelius and Dulong's value, 0·764 for C : O, with Dumas and Stas's 0·7500. Prominent amongst these chemists are Lothar Meyer and Seubert, who, in a memoir published by them in the *Ber. Deut. Chem. Gesell.* in March, 1889, give expression to their conviction in the most emphatic manner possible by insisting that we must henceforth refer our atomic weights not to O = 16, but to O = 15·96, for " dieser Wert ist der am meisten verbürgte und desshalb allen übrigen für diese Grösse Betracht kommenden vorznziehen." But where are the guarantees? A glance at Lothar Meyer and Seubert's book* affords an answer, inasmuch as it clearly shows that their conviction of the correctness of their number is based chiefly upon Dumas's and upon Erdmann and Marchand's quantitative synthesis of water, which both, in their hands, led to the identical value, 15·96 for O : H. But, unfortunately, their calculations rest on a false basis. Their mode of calculating Dumas's determinations is that, viewing his nineteen syntheses as *quasi* one synthesis, they deduce the value O : H from a combination of the sum of Dumas's nineteen oxygen weights with the sum of his nineteen uncorrected water weights, which comes to pretty much the same thing as if they had calculated the constant from the mean of Dumas's " equivalents bruts," meaning the equivalents as they come out, if we neglect the adventitious water produced by the dissolved oxygen in the sulphuric acid used for making the hydrogen. But Dumas, as we see from his memoir, effected the corresponding correction in each of the nineteen cases; and, if we believe in Dumas's work at all, what right have we to discard his corrections on his own numbers? Clearly, none whatever; we must go by his "equivalents corrigés," and their men is 0·12515, corresponding to O : H = 15·98.

To pass to Erdmann and Marchand; they, as Lothar Meyer and Seubert inform us, made eight syntheses, which, if calculated as one synthesis, lead to the value 15·96. But, when we look at the original memoir, we find that E. and M. made two distinct sets of four experiments each. In the first set they weighed their oxide of copper and metallic copper in the ordinary way, and allowed for the displaced air by calculation; in the second they adopted Dumas's plan, and weighed both the oxide and the metal derived therefrom in the same evacuated tube. And in each of these four latter experiments (as also in one of the first series) they took care to free their hydrogen from every trace of atmospheric oxygen by making it pass through a red-hot tube full of metallic copper, and from it through a U-tube charged with fused caustic potash before it reached its destination. In other words, while Dumas corrects for his adventitious water by calculation, they avoid its formation. Their general mean for the weight of water containing one part of oxygen, that is to say, for $H_2O$ : O, is 1·12520. But, obviously, their second series is far more reliable than their first, and its mean stands at 1·12492, corresponding to O : H = 16·010. And these four determinations, being obtained by a decided improvement upon Dumas's method, are worth as much as Dumas's nineteen; hence the nett result of the two investigations taken conjointly is—

O : H = ½ (15·981 + 16·010) = 15·996,

or, practically, the exact number, 16·000.

But, supposing even we had nothing but Dumas's uncorrected equivalent to go by, seeing that the nineteen individual values for O : H, as calculated from these, vary from 15·89 to 16·02, it surely is worse than pedantry to swear to that 15·96 as if it were a revelation from heaven! So I thought, some months ago, when, on the basis of little more than a second-hand knowledge of the two researches, I came to speculate on the matter; and, being moreover imbued with a strong mental bias in favour of Prout's law, I decided upon undertaking an experimental inquiry into Dumas's method-errors, feeling sure in my own mind that I should be able to prove that the old integer 16 is at least as good an approximation to the truth as the fashionable 15·96.

As a first step, I directed Mr. Henderson to set up as close an imitation as possible of Dumas's apparatus for the production of pure hydrogen, and then to determine the oxygen in what we soon came to call "Dumas hydrogen," by filtering a sufficient known volume of the gas through red-hot copper gauze, and weighing the water produced. The result more than confirmed my anticipation, but, while Henderson experimented, I studied Dumas's and Erdmann and Marchand's original memoirs and made an unexpected discovery.

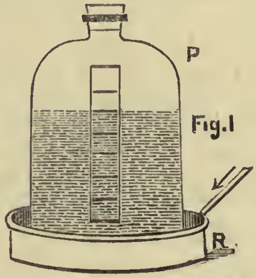

Fig. I

From Dumas's account it appears that, while he weighed his oxide of copper and oxide *in vacuo*, he weighed his water in the air, and that, consequently, his water-weights were liable to be reduced to the vacuum. That a man like Dumas should be capable of omitting this obviously very relevant correction would appear to be an absurd presumption, but the way in which he states his results (on page 200 of his memoir) tends to confirm it. On the table referred to he gives, in so many successive columns, (1) the weight of the water-receptacle before, (2) after the experiment, (3) the exact difference of the two weights as " the weight of water produced," (4) the value $H_2$ : O as calculated from the recorded weights of water and oxygen, and (5) the same corrected for the oxygen introduced as dissolved air with the dilute acid used for the evolution of the hydrogen, as the " equivalent corrigé." Now, if Dumas puts us in a position to check his subtractions, then, assuming that the weighings (1) and (2) as they stand are already reduced to the vacuum, he is surely bound to tell us how he calculated the respective corrections. But he does nothing of the kind. Assuming, as I did at the time, that he simply forgot the vacuum correction, all we can do now is to add to his mean equivalent of hydrogen the weight of air, displaced by 1·12515 parts of water. Assuming, as we may without fear of committing a serious error, that the mean density of the air in which he operated was the same as that corresponding to 15° C. and 760 m.m. pressure, we arrive at the value 0·00138, which raises the equivalent of hydrogen to 0·12653, corresponding to O : H = 15·81! But, admitting this to be the real result of Dumas's determinations, how is it that Erdmann and Marchand, who *did* reduce their water-weights to the vacuum (there is no doubt about this, because they give us in each case both the uncorrected and the corrected number), arrived at the value 16·01?

In going carefully over their report, I, at last, come to see my way towards a plausible explanation. As appears from their memoir, they dried their hydrogen finally by passing it through a U-tube, 3 feet long, charged with caustic potash, which, they assure us, dehydrated even a quick current of the gas completely; " because a U-tube filled with fused chloride of calcium, if appended to the outlet end of the potash tube, suffered no change of weight." Their water receptacle was combined with two chloride of calcium tubes to retain the moisture of the

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* " Die Atomgewichte der Elemente, aus den Originalzahlen neu berechnet, von L. M. and S." 1883.

surplus hydrogen and of the air which was sent through the apparatus at the end of an experiment. They obviously considered it necessary to prove that fused caustic potash dries a gas completely, but they had no doubt about the efficiency of fused chloride of calcium: and this is no more than was at the time admitted by every chemist. But Fresenius (see his *Zeitschrift* for 1865, p. 177) has since shown that a moist gas, after having been dried exhaustively by even fused chloride of calcium, gives up a quantity of water to oil of vitriol, which, in his trials, amounted to about 1 m.grm. per litre of gas. Now, Erdmann and Marchand's test experiment with their potash tube is quite compatible with the assumption that this tube retained every trace of moisture from the hydrogen which streamed through it, and it is not unfair to assume that the chloride of calcium which Erdmann and Marchand used *in their actual syntheses* was about at a par with Fresenius's preparation. If I am right so far, it follows that Erdmann and Marchand lost about 1 m.grm. of water for every litre of permanent gas which passed through their water receptacle at the end of the experiment; and this, as a little reflection shows, is amply sufficient to account for all the difference between their value for $H_2O:O$ and Dumas's as corrected by me. But this, as I could not help seeing, would only prove that Erdmann and Marchand's determinations must be given up as hopelessly wrong, and, in any case, it still devolved upon me to prove the correctness of my suspicion concerning Dumas's calculations. Obviously, what I had to do was to inquire critically into both Erdmann and Marchand's and Dumas's methods, and besides to carry out at least a few syntheses of water according to Dumas's method, to enable myself to decide between his own and my mode of interpreting his numbers. And these "few test syntheses" were sure to develop into an independent re-determination of the constant. After some hesitation, I decided upon carrying out this programme, and thanks to the indefatigability and youthful energy of my excellent collaborator, the work was completed in less time than I thought it would demand.—W. D.

(To be continued).

## MANURIAL EXPERIMENTS WITH TURNIPS.[*]

By C. M. AIKMAN, M.A., B.Sc., F.R.S.E.,
Lecturer on Agricultural Chemistry, Glasgow and West of Scotland Technical College, and Glasgow University Extension Board.

The experiments about to be described were carried out in 1889, and had for their object the testing of the value of basic slag as a turnip manure. In order to make the results as valuable as possible, the experiments were carried out on farms in different parts of the West of Scotland; and the author would take this opportunity of expressing his great indebtedness to those gentlemen who so kindly co-operated with him in carrying them out, and for the time and trouble they were good enough to place at his disposal. It is quite unnecessary to say a single word in explanation of what basic slag is. Most farmers have heard a good deal during the last year or two regarding it. The very successful results obtained by its use on the Continent—especially in Germany—have drawn the attention of many of our farmers to its claims as a valuable source of phosphatic manure. But the British farmer is a cautious man, and the mere fact of a manure finding favour with the German farmer is, of itself, not sufficient guarantee to his mind to warrant him following suit. This caution is undoubtedly commendable. No farmer ought certainly to use a manure he is not convinced will repay him. He ought, however, to endeavour to ascertain the value of any great new source of manure as soon as possible. Unfortunately the opportunities and facilities he enjoys for testing the value of new manures are in this country not so numerous as are desirable, and the ultimate result of this extreme caution may be that a cheap and valuable manure may be allowed to be neglected, or it may be sent abroad for use there.

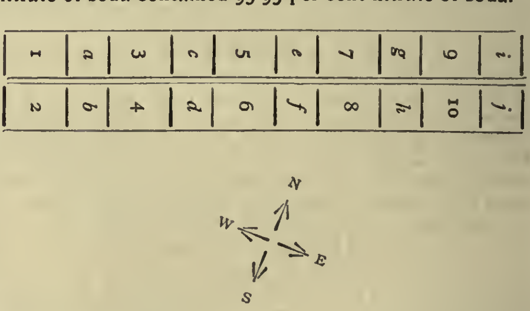
The rapidity with which basic slag found its way into the German agricultural markets was undoubtedly due to the fact that the German farmer, unlike the English farmer, enjoys exceptional advantages, in the facilities he possesses, for having any new manure tested. Germany, with its magnificently equipped experimental stations scattered throughout the length and breadth of the land, is not long in providing herself with the desired information.

When we consider that basic slag is chiefly produced in this country, that it is to be had in very large quantities and at a very moderate price,[*] it does seem highly desirable that in the interests of our agriculture very many more attempts should be made to ascertain whether it really is a cheap and valuable form of phosphatic manure for our British soils, and whether it is in our interests to allow it to be entirely exported to Germany instead of using it ourselves.

The slag used in these experiments was of quality, so far as I am aware, hitherto unexperimented with, except in North Wales, where it was used last year at my suggestion in some experiments carried out by my friend Professor Dobbie, of Bangor. It contained of phosphoric acid only 8·55 per cent (=tricalcic phosphate of lime, 18·66 per cent), and its mechanical fineness was such that 56 per cent passed through the regulation sieve. The price of this slag would be, I am informed by the makers, so cheap that if it is shown to possess any fair manurial value, it would be for the farmer an extremely cheap source of phosphoric acid.

The experiments were intended to be carried out on the same scale in each of the series, but owing to circumstances a slight difference exists in certain cases. The aim of the experiments was to test the slag, first, alone in different quantities, and against superphosphate; secondly, with farmyard manure as against "super" and farmyard manure; and thirdly, with farmyard manure and nitrate of soda, as against super and nitrate of soda with farmyard manure; and the whole of the unmanured plots were tested against plots which received no manure.

The superphosphate and nitrate of soda, used in all the experiments, were the same. The superphosphate contained 29·62 per cent "soluble" phosphate; while the nitrate of soda contained 95·95 per cent nitrate of soda.



The first series of experiments were those carried out on the farm of Mr. John Gilchrist, of Orbiston Mains, Bellshill, Lanarkshire, to whom any value the experiments possess is largely due.

The experiment plots were twenty in number, situated near the centre of a large field with a good exposure, and

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[*] From the *Transactions of the Highland and Agricultural Society of Scotland.*

[*] We should be able to purchase it cheaper than the Germans do, who so largely export it from this country.

well removed from any hedge. The plots were arranged in two rows, ten plots in each row. Ten of the plots measured each the 1-20th of an acre, while the other ten were each 1-480th of an acre. The latter ten plots received no manure, and lay between the manured plots. The object of having so many was to minimise as much as possible errors due to the natural inequalities of the soil.

The accompanying diagram will serve to show the arrangement of the plots.

The breadth of each plot was six drills, equal to about five yards. The soil is described by Mr. Gilchrist as "deep and alluvial on the south-east plots (viz., Nos. 1 and 2), somewhat stiffer on the middle plots, and on the north-west plots looser and more friable." The field, I should add, slopes to the south-east. The following is Mr. Gilchrist's statement of the history of the field during the previous five years in respect to the manures applied and crops grown:—

| Year. | Crop. | Nature. | Manure. |
|---|---|---|---|
| 1883. | Potatoes. | Of good quality. | Farmyard manure. |
| 1884. | Wheat. | Heavy crop. | Nothing. |
| 1885. | Hay. | Good crop. | Nothing. |
| 1886. | Hay. | Heavy crop. | Police manure. |
| 1887. | Hay. | Fair crop. | 1 cwt. nitrate of soda and 1 cwt. salt per acre. |
| 1888. | Oats. | Extra heavy crop. | Police manure. |

The plots were manured as follows:—

Nos. *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, *j*, received nothing.

No. 1 received *basic slag* at the rate of 14 cwt. per acre.

No. 2 received *superphosphate* at the rate of 9 cwt. per acre.

No. 3 received *basic slag* at the rate of 7 cwt. per acre.

No. 4 received *superphosphate* at the rate of 4½ cwt. per acre.

No. 5 received *basic slag* at the rate of 14 cwt. per acre, and *farmyard manure* at the rate of 20 tons per acre.

No. 6 received *superphosphate* at the rate of 7 cwt. per acre, and *farmyard manure* at the rate of 20 tons per acre.

No. 7 received *superphosphate* at the rate of 4½ cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 8 received *basic slag* at the rate of 7 cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 9 received *basic slag* at the rate of 14 cwt. per acre, *farmyard manure* at the rate of 20 tons per acre, and *nitrate of soda* at the rate of 1 cwt. per acre.

No. 10 received *farmyard manure* at the rate of 20 tons per acre.

The experiments were carried out with *Aberdeen yellow turnips*, which were sown on the 21st of May, during favourable weather, and which brairded well. All the manures, with the exception of the nitrate of soda, were spread, or sown in the drills along with the seed. The farmyard manure was spread in the bottom of the drills, the slag and the superphosphate put on the top of it. The drills were then covered and sown the same evening. The nitrate of soda was applied as a top-dressing on the 12th of July (*i.e.*, some seven weeks after sowing). The weather after sowing was pretty dry. The crop was entirely free from turnip-fly.

When visited on the 26th of July the plots which had received dung showed best, but between the remaining plots there seemed to be very little apparent difference. The slag seemed to tell best on the *lightest* soil. Mr. Gilchrist informed me that the plots which did not receive dung were some fourteen days later in being singled than the plots which did. The moisture carried into the drills along with the dung evidently helped the germination of the seed.

The turnips were lifted and weighed on the 18th of November. The following were the results. The weights do not include tops, which were not weighed.

I shall give the yield of the nothing plots first of all.

| No. | Tons. | Cwt. |
|---|---|---|
| *a* .. .. .. .. | 18 | 17 |
| *b* .. .. .. .. | 14 | 0 |
| *c* .. .. .. .. | 14 | 11 |
| *d* .. .. .. .. | 9 | 8 |
| *e* .. .. .. .. | 14 | 2 |
| *f* .. .. .. .. | 14 | 2 |
| *g* .. .. .. .. | 17 | 11 |
| *h* .. .. .. .. | 15 | 0 |
| *i* .. .. .. .. | 12 | 17 |
| *j* .. .. .. .. | 13 | 5 |
| Total .. .. | 143 | 13 |

giving an average of 14 tons 7 cwt.

The discrepancy in the results of these nothing plots strikingly exemplifies the necessity of taking into account the inequalities in the soil, and the peculiar difficulties in the way of arriving at satisfactory results in this kind of experimentation.

The results of the manured plots are as follows:—

| No. | Manure. | Yield of turnips per acre. Tons. | Cwt. | Increase over nothing plots Tons. | Cwt. |
|---|---|---|---|---|---|
| 1. | 14 cwt. slag .. .. .. .. .. | 21 | 10 | + 7 | 3 |
| 2. | 9 cwt. super .. .. .. .. .. | 18 | 5 | + 3 | 18 |
| 3. | 7 cwt. slag .. .. .. .. .. | 13 | 5 | − 1 | 2 |
| 4. | 4½ cwt. super .. .. .. .. | 11 | 15 | − 2 | 12 |
| 5. | 14 cwt. slag, 20 tons dung .. | 22 | 5 | + 7 | 18 |
| 6. | 7 cwt. super, 20 tons dung . | 22 | 0 | + 7 | 13 |
| 7. | 4½ cwt. super, 20 tons dung, 1 cwt. nitrate of soda .. | 24 | 10 | +10 | 3 |
| 8. | 7 cwt. slag, 20 tons dung, 1 cwt. nitrate of soda .. | 24 | 10 | +10 | 3 |
| 9. | 14 cwt. slag, 20 tons dung, 1 cwt. nitrate of soda .. | 25 | 10 | +11 | 3 |
| 10. | 20 tons dung . .. .. .. | 22 | 10 | + 8 | 3 |

The above results call for some remarks. In the first place it will be noticed that plots Nos. 3 and 4, respectively manured with 7 cwt. of slag, and 4½ cwt. of super, instead of showing an increase over the nothing plots, show a decrease of 1 ton 2 cwt. in the one case, and 2 tons 12 cwt. in the other. In noticing this I was first inclined to think that the inequality in the yield of the nothing plots might explain it. I find, however, that on looking at the nothing plots adjoining these two plots, while in the case of No. 4 they do help to explain the anomaly, in the case of No. 3 they, on the other hand, increase it. With regard to the other plots it will be seen that No. 9 shows the largest increase, viz., 25 tons 10 cwt., or an increase over the average of the unmanured plots of 11 tons 3 cwt.,—*i.e.*, an increase of over 77 per cent. This plot, as will be seen from the table, was manured with 14 cwt. slag, 20 tons dung, and 1 cwt. of nitrate of soda per acre. The plots which show the next largest increase are Nos. 7 and 8, viz., 24 tons 10 cwt., or an increase over the average of unmanured plots of 10 tons 3 cwt.—*i.e.*, about 70 per cent of an increase. These plots received the same quantities of dung and nitrate of soda as No. 9, and 4½ cwt. of super, and 7 cwt. of slag respectively.

In summing up these results, and attempting to draw some practical conclusions from them, we may estimate the money value represented by the increase of crop obtained by the use of the manures; then calculate the money value of the manures applied, and by deducting the latter from the former, ascertain what the profit amounts to. Secondly, we may estimate the unitary value these experiments show phosphoric acid to possess in the form of basic slag and superphosphate respectively. The following table shows side by side the cost of the manures and the value of the increase in crop. The slag is calculated at £1 per ton, the super at £2 15s. 6d., the nitrate of soda at £10 per ton, and the dung at 6s. per ton:—

| No. | Manure. | Cost. | Value of increase of crop. |
|---|---|---|---|
| 1. | 14 cwt. slag .. .. .. .. | £0 14 0 | £5 0 0 |
| 2. | 9 cwt. super .. .. .. .. | 1 5 0 | 2 15 0 |
| 5. | 14 cwt. slag and 20 tons dung .. .. .. .. | 6 14 0 | 5 11 0 |
| 6. | 7 cwt. super and 20 tons dung .. .. .. .. | 6 19 0 | 5 6 0 |
| 7. | 4½ cwt. super, 20 tons dung, and 1 cwt. nitrate of soda.. .. | 7 2 0 | 7 2 0 |
| 8. | 7 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda.. .. | 6 17 0 | 7 2 0 |
| 9. | 14 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda.. .. | 7 4 0 | 7 16 0 |
| 10. | 20 tons dung .. .. .. | 6 0 0 | 5 14 0 |

*N.B.*—The turnips were sold for 14s. a ton.

From the above figures it will be seen that the only plots showing a clear profit are Nos. 1 and 2, which received slag and super alone. In the case of plots Nos. 8 and 9, which received dung and nitrate of soda in addition, there is, it is true, a slight profit; while in the case of No. 7 the cost of the manures and the value of the increase of crop balance each other. It will be seen in this case that the dung applied in such large quantities does not repay itself. Of course it must be borne in mind that the effect of the dung will not merely be felt during the first year, but also throughout most of the rotation. Still, while this is doubtless true of the dung, it may also be argued that it is likewise true to a certain extent of the slag.

On the whole, therefore, it would seem that the application of farmyard manure in such large quantities is not economical. Comparing plots Nos. 1 and 10, which received 14 cwt. slag and 20 tons dung respectively, we find that the increase in crop is practically the same, although the difference in the cost of the manures applied amounts to £5 6s.

A comparison of plots Nos. 5, 6, and 10 shows that even an application of 20 tons of farmyard manure alone constitutes in this case an excessive mineral manuring, since the addition of 14 cwt. slag and 7 cwt. super respectively produces no increase. That, however, this does not apply to the same extent to nitrogen, plots Nos. 7 and 8 seem to indicate. In the case of these two plots it will be seen that the addition of 1 cwt. of nitrate of soda increased the value of the yield nearly £2 per acre.

In conclusion, it must be admitted that the value of these experiments is considerably impaired by the fact that the rate at which the manures have been applied is excessive. As, however, many farmers apply manures very much on the same scale, these results cannot fail to possess considerable interest for many.

The next series of experiments were carried out on the farm of Mr. George Graham, Easterboard, Croy, in the county of Dumbartonshire. The experiments were carried out on a clayey soil, and each plot was one-tenth of an acre in extent. The field possesses a fair southern exposure, the plots were each 2¼ yards broad, consisting of three drills. They ran from north to south—to within 6 yards of the top of the field, where there is a very ragged hedge, and to the foot of the field, where there is a ditch, separating it from the adjoining field.

The soil is described by Mr. Graham as "rather clayey, with a white moorish sand in it; altogether a poor soil, and has always required very liberal treatment to raise good crops." A carefully selected sample of the soil was analysed before the commencement of the experiments, and the following are the results:—

(*a*) Mechanical analysis—

| | |
|---|---|
| Clay .. .. .. .. .. | 79·91 per cent |
| Sand .. .. .. .. .. | 20·09 ,, |
| | 100·00 |

(*b*) Chemical analysis (soil dried at 212° F.)—

| | |
|---|---|
| Organic matter* .. .. .. .. .. | 10·633 |
| Iron sesquioxide and alumina.. .. | 9·000 |
| Lime .. .. .. .. .. .. .. .. | 0·504 |
| Magnesia .. .. .. .. .. .. .. | 0·366 |
| Potash.. .. .. .. .. .. .. .. | 0·141 |
| Soda .. .. .. .. .. .. .. .. | 0·307 |
| Sulphuric acid .. .. .. .. .. .. | 0·078 |
| Phosphoric acid.. .. .. .. .. .. | 0·185 |
| Insoluble siliceous matter, chlorine, carbonic acid, &c... .. .. .. | 78·786 |
| | 100·000 |

* Containing nitrogen 0·232.

The past history of the field is described by Mr. Graham as follows:—"It was green cropped in 1880 with turnips, and got liberal manuring (25 to 30 tons), with City of Glasgow police manure. The crop of turnips was very poor; but the succeeding oat crop was fair, and the hay crop in 1882 was also a fair crop. In the summer of 1883 it was eaten by cattle till the middle of June, and then left to grow hay, which was mown about the end of July.

It has been in grass ever since, till last year, when there was a crop of oats on it, which was poor, with the exception of a small piece at the top of the field, which was good." I forgot to add that, with regard to the situation of the field, the north side is a very little higher than the south, and that a slight elevation takes place two-thirds of the way down the field, so that one part lies to the south and another to the north. As, however, each plot extends the whole length of the field, this inequality is shared equally by every plot.

The field was deeply ploughed with Oliver's chilled plough about the end of November. It was wrought into a fine tilth just before drilling. The drills were opened on the 27th of May, the farmyard manure spread in, and the slag, superphosphate, and the nitrate of soda were sown with the hand the same day. The drills were then closed, and the turnips were sown the following morning before seven o'clock, rain beginning to fall before the sowing was finished. The ground was in good order, and other circumstances were favourable—rain and heat continuing for several days. The kind of turnip used in this experiment was Drummond's Improved Aberdeen Green Top Yellow. The following is a statement of the quantities of manures applied per acre:—

| Plot No. | |
|---|---|
| 1. | Nothing. |
| 2. | 4 cwt. super. |
| 3. | 8 cwt. super. |
| 4. | 6 cwt. slag. |
| 5. | 12 cwt. slag. |
| 6. | Nothing. |
| 7. | 6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda. |
| 8. | 6 cwt. slag and 15 tons dung. |
| 9. | 12 cwt. slag and 15 tons dung. |
| 10. | 12 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda. |
| 11. | Nothing. |

The following are the notes supplied me by Mr. Graham:—"June the 5th. The turnips brairded; the ground at that time being very much battered with rain, and caked on the top. At the end of June the turnips were thinned—all, at any rate, with the exception of No. 1 (nothing plot), which was not ready for thinning till the 11th of July. On that date the plots showed as follows:—

Nos. 7 and 10—those which received slag along with dung and nitrate of soda—looked best.

Plots Nos. 8 and 9—those which had received, along with the slag, dung—were next best in appearance, and only slightly inferior to Nos. 7 and 10.

Plots Nos. 2 and 3—those which had received superphosphate in larger and smaller quantity respectively—came next in order, looking considerably poorer, but differing very little from one another.

Plots Nos. 4 and 5—those which had received slag in larger and smaller quantity respectively—came next in appearance, and did not seem to differ in appearance from one another.

Plots Nos. 6 and 11—those which received nothing—came last." With regard to these two plots, Mr. Graham remarks that they each received a small portion of the slag which was blown over, when being sown in the adjoining plots, and that they can scarcely be regarded as "fair" nothing plots.

(To be continued).

## NOTICES OF BOOKS.

*Our Secret Friends and Foes.* (Expanded from Lectures delivered before Popular Audiences in London, Edinburgh, and elsewhere). By Percy Faraday Frankland, Ph.D., B.Sc., F.R.S., F.C.S., &c. Society for Promoting Christian Knowledge. London: Northumberland Avenue. 1893. Pp. 167.

For a long time the intelligent part of the public has felt the want of a manual of bacteriology, popular, yet at the same time accurate, and on a level with the present state of Science. Dr. P. F. Frankland has most ably supplied this want, and has thereby rendered a serious service to Science in general and to hygiene in particular. The notions of the public concerning bacteriological research and its possible results have been hitherto hazy in the extreme. It has been made the subject of pointless jokes by the "witling gallants" of the literary and the political press. It has been execrated by mœnads and zöophilists, and it is even yet slighted by a few physicians of eminence who owe their success, in fact, to what may be called "rule of thumb,"—a certain incommunicable tact. To all these classes of gainsayers Dr. Frankland offers valuable lessons, if his readers will only take them to heart.

The author gives us first a general account of the structure and the classification of these ultra-microscopic organisms, bacilli, spirilla micrococci, collectively spoken of as *bacteria* as well as the *yeasts* and the *moulds*. He describes the formation of spores—the reproductive forms of many species,—justly characterised as the hardiest forms of living matter which Science has yet revealed, since they are "unaffected by cold far greater than that of an Arctic winter," and can sometimes even survive a few minutes exposure to boiling water.

The second chapter is devoted to the micro-organisms of the air, and involves an account of the long controversy on the alleged "spontaneous origin of life," or abiogenesis. The controversy was finally decided by Pasteur and Tyndall in such a manner as to fully confirm the aphorism of Hunter, "Omne vivum ex ovo." Dr. Frankland duly calls attention to the comparative paucity of microbia at great altitudes, on sea at great distances from land, and in undisturbed air. Mention is made of *Bacillus prodigiosus*, which sometimes turns bread of a blood-red colour, and occasioned in the dark ages the dreaded portent of the "bleeding host," sometimes used as a pretext for the immolation of Jews, witches, and heretics. The study of the air-dwelling micro-organisms is mentioned as having led the way to Sir Joseph Lister's great discovery,—the antiseptic treatment of wounds.

We come next to the micro-organisms of water. Here are described the surprising results of filtration. The importance of drinking-water in reference to public health is truthfully asserted to have been first established and taught in Britain, even before the microbial theory of disease was established.

"Useful Micro-organisms" is the title of a highly instructive chapter. Passing over the part played by certain *Saccharomyces* in the production of alcohol—a function which certain reformers think is a mistake in creation—we come to the question of nitrification, *i.e.*, the conversion of the inert nitrogen of the air into nitric acid, in which state it becomes available as plant-food. In discussing the fixation of nitrogen we find no mention made of the researches of M. Georges Ville, who certainly has taken no unimportant share in demonstrating the action of atmospheric nitrogen in the nutrition of vegetables.

It is curious that the two bacteria which respectively convert ammonia into nitrous acid and nitrous acid into nitric acid, require a culture-medium of silica in the gelatinous state. This little fact may yet be found to have an unimagined importance. The author considers that at the epoch when the nitrate beds of Chili and Peru were formed, the nutrifying organisms were much more powerful than those now existing.

Micro-organisms are shown to be gradually assuming the character of chemical reagents. At the same time Dr. Frankland shows two things: That among members of a "pure culture" there may be individual differences, and that they may be modified by cultivation. Here the author writes under Darwinian inspiration, and finds one of the most interesting evidences of Evolution, as it has been experimentally shown by Dr. Dallinger, F.R.S.

We next come to the malignant or pathogenic organisms, the producers of cholera, typhoid, small-pox, diphtheria, rabies, and doubtless of all the communicable diseases. Prominent mention is made of the infectious character of pulmonary consumption. It is a sad fact that an Australian physician who anticipated Koch in this striking discovery reaped in return, not honours but something very like persecution. The populace of Melbourne was enraged at being told that their climate was not a specific for tubercular disease.

The bacillary character of tetanus or lock-jaw, established by Kitasato, a Japanese pupil of Prof. Koch, is of the greatest importance. A case is mentioned of a child dying of tetanus in consequence of some cobwebs having been applied to stop the bleeding from a cut. Spores of tetanus had become entagled in the web, and had set up the dreadful infection. The tetanus bacillus haunts garden soil, the mud of swamps, &c. Hence we need not wonder that tetanus ensues upon wounds received from the arrows of certain African and Oceanic savages. The points of the arrows are poisoned by dipping them in the mud of swamps and allowing them to dry in the sun.

This chapter is aptly closed with an expression of regret that in the development of preventive medicine England has unfortunately lagged behind, as it is all but impossible at the present time to carry out the necessary investigations in this country. No names are mentioned, whether of individuals or of organisations, but it is impossible to mistake the allusion. We hope that Dr. Frankland is not mistaken in his confidence that the public mind is beginning to recover from the hysterical delusions with which it has been "chloroformed."

One of the lessons of this book is the exceptional fruitfulness of boundary lines. The study of the micro-organisms lies on the mutual frontiers of biology and chemistry, and its cultivation has proved most remunerative. We trust that this invaluable book will receive the wide and thorough appreciation which it merits.

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*The Framework of Chemistry.* Part I. *Typical Facts and Elementary Theory.* By W. R. Williams, M.A. London: G. Bell and Sons. 1892. Pp. 48, 8vo.

This little book would be very useful if it had not quite so many predecessors in the same field. It has one creditable peculiarity which should not be overlooked; it is not written down to the requirements of students preparing for any examination.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 3, January 16, 1893.

**Phosphorescent Zinc Sulphide considered as a Photometric Standard.**—Charles Henry.—Within wide limits, and consequently under conditions easy to be realised, the quantity of light emitted by phosphorescent zinc sulphide at a given moment is independent of the distance of the magnesium, independent of the time of illumination, independent of the thickness of the layer of sulphide. In a word, phosphorescent zinc sulphide presents in the highest degree the characters required by a secondary photometric standard.

**An Acid Potassium Platonitrite.**—M. Vèzes.—A solution of potassium platonitrite slightly acidulated with any acid occasions after a certain degree of concentration a dark red deposit on the sides of the vessel, consisting of fine crystalline needles, slightly soluble in cold water, but soluble with a yellow colour in hot water. Its composition is $Pt_3O(NO_2)_6K_2H_4+3H_2O$. Hence the red salt is the acid bipotassium salt of an unknown hexabasic acid.

**The Decomposition of Chloroform in Presence of Iodine.**—A. Besson.—The decomposition of chloroform at incipient redness in presence of iodine yields as principal products $C_2Cl_4$ 35 per cent (or 20 per cent on the chloroform employed), $C_2Cl_6$ 20 per cent, and as secondary products $CCl_4$ 15 per cent, $C_6Cl_6$ 10 per cent, $C_4Cl_6$ 8 per cent: the remnant consisting of small quantities of products not separated comprising traces of iodine compounds and a little $C_2HCl_5$.

**Some Ethers of Homopyrocatechine.**—H. Cousin.—Homopyrocatechine forms two methylic ethers, two ethylic ethers, a methylethylic ether, and a diacetic ether.

**Determination of Phosphorus in Irons and Steels.**—Adolphe Carnot.—This paper will be inserted in full.

**The Waste of Nitrogen from Farmyard Manure.**—A. Muntz and A. Ch. Girard.—The authors find that peat litter retains nitrogen better than does straw. The additions to straw litter of copperas and of gypsum do not appreciably reduce the loss of nitrogen. One reason of this is the quantity of fixed bases, alkaline or alkaline-earthy, contained in the excreta of farm animals, especially of horned cattle and sheep. This alkaline matter decomposes the ferrous sulphate to such an extent that at least 700 kilos. of the ferrous salt would be required yearly per head of horned cattle to arrest the escape of ammonia.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxi., Part 5.

**An Improved Calorimeter.**—F. Fischer (*Zeit. Angew. Chemie*).

**An Automatic Sprengel-Pump.**—H. T. Wells (*Ber. Deut. Chem. Gesell.*).—Both these papers are useless without the accompanying figures.

**Agitating Machine for the Analysis of Superphosphates.**—O. Güssefeld (*Zeit. Angew. Chemie*).—This note requires the accompanying figures.

**Blast for Carburetted Air.**—M. Pauquelin (*Comptes Rendus*).

**The Preservation or the Purification of Some Reagents.**—W. Hampe (*Chem. Zeit.*).—As regards the preservation of hydrofluoric acid in bottles, &c., of vulcanite, the author states that organic substances may easily be taken up by the acid from the material of the bottles, so that after some time it distinctly decolourises solution of permanganate. In determining ferrous oxide in silicates, this circumstance may render the results too high. Hampe, therefore, for such determinations, recommends a previous addition of sulphuric acid and permanganate until a permanent red colour appears, after which the acid may be safely used. Hydrofluoric acid also takes up alkalies from some kinds of vulcanite. To avoid both these impurities, Hampe uses platinum bottles holding about 1 kilo., which, as a protection against injuries, are inclosed in a closely fitting copper flask, closed with a screw. For preparing non-arsenical sulphuretted hydrogen, Hampe, in case of ordinary analyses, considers it sufficient to cause the gas to traverse two or three receivers, containing either soda or sodium sulphide. In very accurate operations, Hampe obtains sulphuretted hydrogen from pure crystalline sodium sulphide and dilute sulphuric acid (1 : 10) which has been tested in Woolf's apparatus. The solid salt, along with a little water, is placed in a Woolf's bottle of medium size, one tubulure of which has a funnel tube fitted with a cock, whilst the other tubulure admits the gas-delivery pipe. The dilute sulphuric acid is introduced through the funnel tube in suitable quantity. The gas traverses a washing bottle of pure water or a solution of soda. In order to remove hydrochloric acid from chlorine gas (important in Woehler's process for determining total carbon in iron), Hampe uses a watery solution of permanganate, and allows the gas to traverse the washing liquor in small bubbles. The colour shows whether it is fit for use. The washing bottle is placed between the generating-vessel and the drying apparatus.

**An Indicator in Alkalimetry.**—Werner Bolton (*Zeit. Angew. Chemie*).—Especially in cases where the operation has to be performed by workmen, the author instead of dyes, which change colour, uses a concentrated solution of flower of sulphur in an alkaline sulphide. Of this solution a drop is added, and a corresponding quantity is deducted from the total acid consumed, or the liquid is stirred with a glass rod which has been dipped in the solution of alkaline sulphide. The solution is heated to ebullition and titrated. As soon as a milkiness appears in the liquid, which does not disappear on vigorous agitation, the operation is complete. The indication is better marked than that with litmus or turmeric.

**The Analysis of Ferrochrome, Ferroaluminium, Ferrotungsten, Ferrosilicon, and Ferrotitanium.**—A. Ziegler (*Dingler's Jour.*).—Already inserted.

**Analysis of Galena and Lead Sulphate.**—Rudolf Benedikt (*Chem. Zeitung*).—The decomposition of galena can be easily and completely effected by heating with hydriodic acid. The pulverised mineral is covered with some water in a hemispherical porcelain capsule, and then with a few c.c. of commercial hydriodic acid of 1·7 specific gravity. If the moistening with water is omitted there ensues a violent effervescence. The capsule is covered with a watch glass and heated on the water-bath. In a few minutes the lead sulphide is completely converted into lead iodide. The watch glass is removed, rinsed off, and evaporated to dryness. The residue when cold is covered with dilute nitric acid, the capsule is covered and heated on the water-bath. The nitric acid decomposes the lead iodide, with liberation of iodine. As soon as the oxidation is at an end the capsule is uncovered, the contents evaporated to dryness, the residue is moistened with dilute nitric acid, filtered, and washed out, when the entire lead is in solution as lead nitrate, and may be determined with sulphuric acid in the usual manner.

Lead sulphate is converted into lead nitrate in a similar manner. The substance is covered with a little water in a small beaker, hydriodic acid is added, and a moderate heat applied. In a few minutes the whole is reduced. Sulphur is deposited on the sides of the beaker. When cold, the contents of the beaker are washed with cold water into a capsule, evaporated to dryness, moistened with nitric acid, and further treated as above.

**Process for the Quantitative Separation of Silver and Lead.**—R. Benedikt and L. Gaus (*Chem. Zeit.*).—Already inserted.

**Volumetric Determination of Sulphuric Acid by the Chromate Method.**—K. Farnsteiner (*Chem. Zeit.*).—Already inserted.

**Some Reactions of the Three Isomeric Amidobenzoic Acids.**— Oechsner de Coninck.—(From the *Comptes Rendus*).

**The Execution of Elementary Analyses by Combustion with Oxygen at High Pressure in the Calorimetric Bomb.** — Prof. Berthelot. — (From the *Comptes Rendus*).

**Saponification of Oils and Esters by Sodium Alcoholate.**—K. Obermüller.—A. Kosel and K. Obermüller have formerly observed that as a rule the soda-soap of the existing acid and the free alcohol of the ester are formed. On further studying this process, Kooel and Krüger recognised as intermediate products the compound of the acid existing in the fat with the alcohol of the alcoholate employed, that is the ethyl- or amyl-ester. Latterly K. Obermüller has resumed the subject, and concludes that on assuming that the water present takes part in the reaction, the entire process may be easily explained. The sodium alcoholate forms at first with the glyceride of the fatty acid sodium glycerin and fatty ester. In presence of water the sodium glycerin is decomposed into glycerin and sodium hydroxide, which latter saponifies the ester, forming soda-soap and alcohol.

**Determination of the Carbonyl Oxygen of the Aldehyds and the Ketones.**—H. Strache (*Monats'hefte fur Chemie*).—This paper requires the two accompanying illustrations.

**The Determination of the Strength of Aqueous Solutions of Acetic Acid by means of the Specific Gravity.**—E. Nickel (*Chemiker Zeit.*).—This operation presents a certain difficulty, as the specific gravity of such solutions increases with augmenting concentration only up to 80 per cent, and then decreases. The author overcomes this difficulty by determining the spec. grav. as usual, diluting with water, and determining the spec. grav. again. If the spec. grav. rises, the higher value must be assumed to be correct, but if it falls, the lower.

**The Determination of the Acidity of Milk.**—H. C. Plant (*Archiv. fur Hygiene*).—Already inserted.

**Examination of Vinegar.**—S. A. Vasey.—(From the Chemical News).

**Recognition of Bombay Mace.**—Th. Waage and O. Warburg.—The microchemical reaction with potassium chromate is recommended.

**Process for Examining Commercial Spirits.**—Ed. Mohler (*Ann. Chim. Phys.*).—Already inserted.

**Examination of Safron and Safron Substitutes.**—E. Vinassa (*Archiv. Pharm. Chemie*).—This process is of no practical importance.

**The Determination of Kreatinine in Urine.**—MM. Gautrelet and Vieillard.—Already inserted.

**Method for Determining the Volume of the Corpuscular Elements of the Blood.**—M. and L. Bleibtreu (*Pfluger's Archiv.*).—Not adapted for useful abstraction.

**Detection of Carbon Monoxide in the Blood.**—H. Bertin-Sans and J. Moitessier.—(From the *Comptes Rendus*).

**The Spectrum of Methæmoglobine.**—P. Dittrich and M. Araki (*Archiv. Experiment Pathol.*).—The spectrum contains only two absorption-bands. A solution of pure crystals, if examined in a stratum of 1 c.m. in depth, transmits the red rays up to the wave length of 660, even at a concentration of 3 per cent. Then follows the obscurity corresponding to the well-known methæmoglobine bands, the middle of which coincides with $\lambda = 632$. From these the absorption decreases to about 606, and remains then approximately constant as far as D, and then again increases. The next stage of darkening has its turning-point at 579, corresponding to the absorption-band II. of authors. A further stage of darkening at about 540 occurs not as a band, but as the commencement of a strong diffused absorption, which increases uniformly and takes up the rest of the spectrum. The bands III. and IV. of former researchers, Dittrich was unable to find in solutions perfectly free from oxyhæmoglobine.

**Chemico-Toxicological Detection of Hydrastin.**—Dioscoride Vitali.—He proposes two reactions. If a crystal of hydrastin or a salt of hydrastin is covered with ½ to 1 c.c. of sulphuric acid in a porcelain capsule and stirred with a glass rod, the mass takes a yellow colour, which, on the addition of a granule of saltpetre and stirring with a glass rod, turns to a yellowish brown. If a solution of stannic chloride is added drop by drop, a splendid violet-red colour is produced. If hydrastin in a porcelain capsule is covered with four to six drops of nitric acid, the liquid is heated to boiling and allowed to evaporate at a gentle heat after expelling the nitrous acid. The yellowish residue is turned a dark green if touched with a drop of an alcoholic solution of potassium hydroxide. If the residue when cold is covered with sulphuric acid, it takes an intense violet colour.

**A Revision of the Determination of the Atomic Weight of Copper.**—Th. W. Richards (*Amer. Acad. of Art and Science*).—The mean referred to, $O = 16$, is $Cu = 63\cdot604$.

## MISCELLANEOUS.

**Royal Institution.**—On Thursday next, February 9, Professor Patrick Geddes will begin a course of Four Lectures on "The Factors of Organic Evolution"; and on Saturday week, February 18, The Right Hon. Lord Rayleigh will begin a course of Six Lectures on "Sound and Vibrations."

**Explanation of the Difficult Solubility of Chemically Pure Zinc in Acids.**—Jul. Weeren (*Ber. Deutsch. Chem. Gesell*).—The author assumes that chemically pure zinc, as well as other chemically pure metals, are insoluble in acids because in the moment of their immersion in the acid they are at once enclosed by an atmosphere of condensed hydrogen, which under normal conditions prevents a further action of the acid. In proof of this assumption it is observed that if the atmospheric pressure is reduced the zinc is dissolved.

**An Examination-Paper.**—Some students having expressed a desire to know the correct answer to a recent paper, set for the Intermediate Medicine Examination of London University, a committee of teachers has, after much anxious consideration, ventured to suggest the following replies, in the hope that they may serve as a guide to others who may still have this examination before them.

*Q.* 1.—"If bottles were placed before you containing the following substances: (1) acetamide, (2) toluene, (3) phenol, (4) ethyl iodide, (5) ethylene bromide, (6) bromobenzene, how would you be enabled to identify each of them by noting their appearance, odour, and behaviour when poured into water? How would you demonstrate the presence of nitrogen in the acetamide, and of bromine in the bromobenzene?"

*Answer.*—This question divides into two main heads, viz., (*a*) How would you be enabled to identify certain substances? and (*b*) How would you detect nitrogen and bromine? (*a*) I should adopt one of three courses; I should either read some text-book, or, better, I should attend the lectures of some well-known teacher: or perhaps, best of all, I should ask a Fellow of the Institute of Chemistry. I should thus be enabled to identify the substances. (*b*) The presence of nitrogen in the acetamide is easily shown by boiling a sample with caustic soda and smelling the evolved ammonia, and of bromine in the bromobenzene by passing its vapour over red-hot lime, treating the mass with water, and testing for bromine by liberating it with chlorine water.

*Q.* 2.—"What is the nature of the experimental evidence which has led to the conclusion that tartaric acid is a dihydroxydicarboxylic acid?"

*Answer.*—The nature of the evidence is required. A dibasic acid is characterised by the existence of an acid, as well as of a neutral salt; the presence of hydroxyl groups is inferred from the formation of ethylic and acetylic derivatives, and from the fact that they may be substituted for bromine by the action of silver hydroxide, in a compound containing bromine, of which the constitution has been established.

*Q.* 3.—"The substance obtained by treating glycerol with nitric acid is commonly known as nitro-glycerin" (and commonly spelt with an "e"). "Why is this an incorrect name, and in what respects does the substance differ from a nitro-compound?"

*Answer.*—Before proceeding to infer conclusions it is well to verify premises; the committee therefore investigated the action of nitric acid on glycerin. A mixture of the two substances was made, and after a short time a torrent of red fumes was evolved. The committee then retreated to a convenient distance and focussed a cathetometer on the scene of action. The products were mostly gaseous; the residue contained a little oxalic acid. It assumed, therefore, that oxalic acid is the substance referred to. It is obvious that this body has no claim to the name nitro-glycerin, for it contains no nitrogen; and it may be distinguished from a nitro-compound by its reducing an acidified solution of permanganate.

*Q.* 4.—"How has glucose been prepared artificially? What is the difference in constitution between glucose and levulose?"

*Answer.*—The method of preparing artificially, or of manufacturing glucose, is by boiling rags or starch for some days with dilute sulphuric acid, neutralising the acid with lime, filtering from the gypsum, and concentrating in a vacuum pan. The one is an aldehyd containing the group CHO, and the other a ketone containing the group CO. (This question obviously refers to the synthesis of glucose; but the actual answer is the one given).

*Q.* 5.—"What is the distinction between fatty and aromatic compounds?"

*Answer.*—*The* distinction means, we presume, the chief distinction. The chief distinction between fatty and aromatic compounds is that they are described in different sections of the same text-book. Nowadays, so many ring-compounds are fatty, and so many chain-compounds mostly aromatic, that it may be stated that fatty compounds are aromatic, and that aromatic compounds are fatty.

*Q.* 6.—"Describe the manner in which you would effect the complete oxidation of the alcohol in a dilute aqueous solution, and in which you would separate the resulting acid and convert it into sodium salt. Sketch the apparatus you would use."

*Answer.*—By complete oxidation is meant conversion into carbon dioxide and water. We know of no way of effecting this, except by means of a living organism, and of no organism so suitable for the purpose as that of an habitual toper. We would therefore suggest the following method. Take a toper, provided with an œsophagus, a stomach, intestines, a circulatory system, and lungs, and inject the liquid through the mouth. This will not be difficult, if the alcohol be not too dilute ethyl alcohol. Methyl alcohol requires an habitual drunkard, who may be more difficult to procure. If the alcohol be one of the higher of the series, it may be necessary to inject some ethyl alcohol in considerable amount as a preliminary precaution. Let nature take its course; cause the toper to breathe into a bladder, and expel the expired gases through a solution of caustic soda until it is saturated. Evaporate the solution of sodium carbonate and ignite the residue. The apparatus used is termed a toper. He may be sketched thus:—

An occasional sip,
An habitual nip:
A continuous soak,
A thirst like to choke.

## MEETINGS FOR THE WEEK.

Monday, 6th.—Medical, 8.30.
—— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).
—— Society of Chemical Industry, 8. "Manufacture of Nitric Acid," by Oscar Guttmann. "Detection and Estimation of Lead in Citric and Tartaric Acids," by R. Warrington. "New Form of Laboratory Filter-Press," by C. C. Hutchinson.
Tuesday, 7th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8 "Pottery Glazes; their Classification and Decorative Value in Ceramic Design," by Wilton P. Rix.
Wednesday, 8th.—Society of Arts, 8. "Some Points in the Chemical Technology of Oil Boiling, and New Process for Preparing Drying Oils," by Prof. W. Noel Hartley, F.R.S.
—— Geological, 8.
—— Pharmaceutical, 8.
Thursday, 9th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
Friday, 10th.—Royal Institution, 9. "Some Associated Organisms," by Prof. Charles Stewart, Pres.L.S.
—— Astronomical, 3. (Anniversary).
—— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
—— Physical, 5. (Annual General Meeting). "Recent Determinations of Molecular Refraction and Dispersion," by Dr. J. H. Gladstone, F.R.S. "The Separation and Striation of Gases," by E. C. C. Baly.
Saturday, 11th.—Royal Institution, 3. "Expression and Design in Music," by Prof. C. Hubert H. Parry, M.A.

## TO CORRESPONDENTS.

*Cyanogen.*—The paragraph is full of errors. We do not see the use of reprinting it in the Chemical News.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1733.

# ON A
# METEORIC STONE FOUND AT MAKARIWA, NEAR INVERCARGILL, NEW ZEALAND.*

By G. H. F. ULRICH, F.G.S.,
Professor of Mining and Mineralogy in the University of Dunedin, N.Z.

The specimen described in this memoir was found in the year 1879 in a bed of clay which was cut through in making a railway at Invercargill, near the southern end of the Middle Island of New Zealand. Originally this meteorite appears to have been about the size of a man's fist, and to have weighed four or five pounds, but it was broken up, and only a few small fragments have been preserved. The stone evidently consisted originally of an intimate admixture of metallic matter (nickel iron) and of stony material, but much of the metallic portion has undergone oxidation. Microscopic examination of thin sections shows that the stony portion, which is beautifully chondritic in structure, contains olivine, enstatite, a glass, and probably also magnetite, and through these stony materials the nickel iron and troilite are distributed. The specific gravity of portions of the stone was found to vary between 3·31 and 3·54, owing to the unequal distribution of the metallic particles. A partial chemical examination of this meteorite was made by the author and Mr. James Allen, but the complete analysis has been undertaken by Mr. L. Fletcher, F.R.S., of the British Museum. The analysis, which when finished will be communicated to this Society, has gone so far as to show that the percentage mineral composition of the Makariwa meteorite may be expressed approximately by the following numbers:—Nickel iron 1, oxides of nickel and iron 10, troilite 6, enstatite 39, olivine 44.

# FURTHER RESEARCHES IN CONNECTION WITH THE METALLURGY OF BISMUTH.†

By EDWARD MATTHEY, F.S A., F.C.S.,
Associate of the Royal School of Mines.

In 1886—87 and in 1890 I submitted papers to the Royal Society bringing under notice facts which had come to my knowledge whilst engaged upon the practical extraction of this beautiful metal from its ores, and in its separation from impurities which are always associated with it when in a crude or unrefined state.

### IV.—*Bismuth: Its Separation from Arsenic.*

In a paper dated February 10, 1887 (*Proc. Roy. Soc.*, vol. xlix.), allusion is made to the fact that arsenic is often one of these impurities, and at the same time a method is given by which the separation of this metal from bismuth was then successfully effected.

The process adopted when that paper was read, and for a considerable period subsequently, when working upon bismuth containing arsenic, consisted in removing the arsenic by fusing the arsenical bismuth in contact with metallic iron at a dull red heat and under flux. A compound of iron and arsenic was thus formed and could be removed as a scum,—the disadvantages of this process being, first, loss of bismuth by volatilisation, and, secondly, much loss of time in the manipulation of any large quantity to be treated.

Having occasion, a few months ago, to melt together a large quantity of arsenical bismuth, some 700 or 800 kilos., that is, more than three quarters of a ton, in order to obtain a homogeneous alloy upon which to work subsequently by the process above alluded to, it became evident that when the temperature was raised above the melting-point of bismuth, the surface of the metal being exposed to the atmosphere, arsenical fumes appeared, and that these increased as the temperature of the metal became more elevated, the result being that the arsenic came off in dense white fumes ($As_2O_3$).

The observation of this fact led to further experiments, and it was found that if the surface of the bath of fused arsenical bismuth was freely exposed to the air at a temperature rather higher than its own melting point, and if the molten metal was constantly stirred, it was possible to eliminate the whole of the arsenic alloyed with the bismuth by this simple process of fusion with stirring.

As it is a matter of considerable interest for metallurgists to know, not only that this elimination does take place, but also at what temperature it occurs, a series of experiments have been conducted with a view of determining this accurately.

The work of Roberts-Austen has shown that a thermo-junction is practically the only form of pyrometer that can be used for delicate thermal investigations of this kind, but the question arose which particular thermo-junction should be adopted. Was it well to use the platinum-iridium one as advocated by Barus, or the platinum-rhodium one suggested by H. le Chatelier? My previous work on the alloys of platinum and rhodium, lately published in the *Phil. Trans.*, settled the question in favour of the rhodium-platinum thermo-junction, for I was satisfied that the alloy of platinum with 10 per cent of rhodium is as homogeneous as any known alloy could well be, and is therefore admirably adapted for use as a thermo-junction, pure platinum being the opposing metal. Analysis proved that the alloy operated upon in these experiments contained 0·65 per cent of metallic arsenic.

It will be seen that the melting-point of this alloy of bismuth is 278° C. By raising the temperature of the alloy to 395° C. the arsenic freely sublimates from the bismuth alloy, and at a temperature of 513° C. the whole of the arsenic is eliminated.

A point of much interest in relation to molecular physics became evident in the course of the investigation. Arsenic, as is well known, volatilises at the comparatively low temperature of 180° C., without passing through the molten state. Arsenic is not, however, given off freely from the arsenical bismuth until a temperature of 395° is reached. So that the temperature of dissociation of this alloy, containing 0·65 per cent of arsenic, is 114° C. higher than the melting-point of the mass. It was interesting to determine at what temperature the arsenic would be evolved if the alloy were heated *in vacuo*.

A portion of the bismuth alloy containing 0·65 per cent of arsenic was introduced into a hard glass tube, slightly depressed to its centre, and connected at one end with a Sprengel pump, by which it could be rendered vacuous.

The pyrometric wires were in contact with the metallic alloy and passed to the galvanometer through the opposite sealed end of the glass tube.

Heat being applied, the first indication of the volatilisation of the arsenic, shown by the condensation of a film on the cool part of the tube, occurred at 275° C. When the alloy was quite melted the temperature indicated was 316° C.; arsenic came off freely when the temperature rose to 569° C., condensing in a black mirror.

The metal was then allowed to cool, and its settling-point was found to be 268° C., which corresponds with that of the melting-point of bismuth.

The bulk of the arsenic does not appear to be evolved *in vacuo* at a lower temperature than in air.

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* Abstract of a paper read before the Royal Society, Feb. 2, 1893.

† Paper read before the Royal Society, January 26, 1893.

As regards the industrial application of the process, some ten to twelve tons of arsenical bismuth have already been treated in this very simple way, and it has been satisfactorily ascertained that there is no loss of bismuth by volatilisation with the arsenic.

### V.—*The Separation of Bismuth from Antimony.*

The process hitherto adopted in practice for the separation of antimony from bismuth has usually consisted in a simple fusion at a dull red heat with bismuth oxide or bismuth "litharge"—an operation successful enough as to its results, but one requiring no small amount of skill in manipulation; it is also one by which only small quantities can be treated readily at one time—and moreover, the temperature which is necessary to effect the separation of the antimony involves appreciable loss on account of the volatilisation of the bismuth at a red heat; notwithstanding, many tens of tons of bismuth have, however, been treated under my direction by this process.

In an operation lately conducted, involving the melting of a quantity of bismuth containing about one per cent of antimony, it was found that a peculiar oily film was noticeable rising to the surface of the melted alloy; this film did not form all over the surface of the metal, but appeared to rise as from a boiling centre, and this although the metal was at a temperature very little above its melting-point. A portion of the film or layer was removed and tested in order to ascertain its nature, and it was found to contain a very appreciable proportion of *antimony*. I therefore caused the operation to be continued, stirring the metal from time to time with a dried wood stirrer. In the course of three or four hours, removing the film from time to time, the surface of the melted metal assumed a much brighter appearance, and on carefully testing it at this point, the metal was found to be *absolutely free from antimony*. To confirm this and to ascertain more exactly the conditions under which this separation takes place, a further quantity of impure bismuth was operated upon in a similar manner. This second quantity contained other impurities besides antimony, its analysis being as follows:—

| | |
|---|---|
| Bismuth, by difference .. .. | 96·20 |
| Antimony .. .. .. .. .. .. | 0·80 |
| Tellurium.. .. .. .. .. .. | 0·40 |
| Lead .. .. .. .. .. .. .. | 2·10 |
| Copper .. .. .. .. .. .. | 0·50 |
| Arsenic .. .. .. .. .. .. | traces |
| | 100·00 |

The same simple process of fusion and stirring was again adopted—the quantity being about 350 kilogrms.—and when the same oily film commenced to rise to the surface, the temperature of the molten mass of the alloy was taken by means of the le Chatelier pyrometer. A portion of the film removed showed, on being tested, a percentage of over 30 per cent of antimony. A slightly perceptible fume of arsenic was apparent as volatilising, so proving what I found to be the case in the separation of arsenic by simple fusion. (See *ante*).

The point at which this separation of antimony occurs was found to be about 350° C., and at this temperature the metal was maintained for about five hours.

The evidence of an oxidising action became now much less, and, although a very small amount of antimony was present, there was still a little remaining in the alloy; the temperature, therefore, was slightly raised and maintained at 458° C., as shown by the pyrometer, for about four hours, at the end of which time the bismuth became absolutely free from antimony.

The form in which the antimony separated was peculiar—a transparent glass, consisting of antimony oxide—containing about 10 per cent of bismuth; but, of course, in the removal of the antimony oxide a small proportion of the bismuth was mechanically carried with it, resulting in the production of several very interesting and very beautiful metallurgical specimens.

The great advantage of this process is,—like that of the foregoing separation from arsenic,—its extreme simplicity, the low temperature which renders it possible to work upon very large quantities at one time, and the very small amount of time necessary for this separation in comparison with the process hitherto adopted, and the absence of loss in the bismuth operated upon by volatilisation. It is obvious that where metals can be so easily treated in large quantities, the labour and skill hitherto necessary is very considerably reduced, and there is the additional advantage that the loss attending large operations is minimised.

In this and in my previous papers upon this beautiful metal bismuth, I have been able to point to simple dry processes for its separation from gold, lead, copper, arsenic, and antimony, and all these processes are available for treating with care large quantities at one time. When it is remembered what is involved in having to dissolve any quantity of bismuth in acids, and its subsequent precipitation from solution, it surely will be admitted that much of the difficulty in purifying crude bismuth has been effectively removed, as the methods given have been found possible in practice, and advantageous.

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## ON THE ORIGIN OF COLOUR.

### II. The Colour Scale. Thermo-Relations. The Law of Colour.

By WILLIAM ACKROYD.

(Continued from p. 27).

The question has been asked why a colour scale should be used, and not the spectroscope, in investigations concerning the origin of colour?

A metachromatic scale produced by heat exhibits a natural sequence of colours which are of the same kind as those of bodies to be compared in investigations on the origin of colour. This is its first and most important claim for use to that purpose; it is an expression of colour evolution. I have shown that the changes of colour which it typifies are produced by a gradual and increasing absorption of the less refrangible rays (*Phil. Mag.*, Dec., 1876), and as some of these differences, which are readily appreciated by the eye, are not discernible with the spectroscope, eye observations, of which the colour scale is a record, are preferable to spectroscopic for a comparative study of colour in its relation to chemical constitution. It is well, indeed, it is so, as many of the bodies to be studied are amorphous, opaque, and insoluble in liquids without chemical change. What I take to be the true province of the spectroscope in this investigation will be shown in another paper.

The thermo-relations concerned in these colour changes are of interest, seeing that colour is determined to some extent by temperature. From Neumann's law it follows that grm. molecules of a natural series of compounds containing the same number of atoms will require the same quantity of heat to raise them from absolute zero to the normal temperature. Thus the calories required to bring grm. molecules of the following chromates from 0° to 273° absolute temperature will be—

| | | Calories. |
|---|---|---|
| Lemon-yellow, $MgCrO_4$ .. | $\frac{28{\cdot}8 \times 273 \times 140}{140}$ | $= 28{\cdot}8 \times 273$ |
| Yellow, $ZnCrO_4$ .... .. | $\frac{28{\cdot}8 \times 273 \times 181}{181}$ | $= 28{\cdot}8 \times 273$ |
| Orange-yellow, $CdCrO_4$ .. | $\frac{28{\cdot}8 \times 273 \times 228}{228}$ | $= 28{\cdot}8 \times 273$ |

Or generally, if $a$, $b$, and $c$ are the atomic heats of the elements in a natural series of compounds, and $m'$, $m''$,

| Metachromic scale. | White. | Blue. | Green. | Yellow. | Orange. | Red. | Brown. | Black. |
|---|---|---|---|---|---|---|---|---|
| I. Binary compounds.. | — | — | $PtCl_2$ | $PtCl_4$ | — | — | — | — |
| II. Natural series .. | — | — | — | $MgCrO_4ZnCrO_4$ | $CdCrO_4$ | — | — | — |
| III. Crystallised salts.. | — | — | $CoI,2H_2O$ | — | — | $CoI_2,6H_2O$ | — | — |
| IV. Other compounds— | | | | | | | | |
| *a*. Isomorphous groups | $Al_2O_3$ | — | $Cr_2O_3$ | $Fe_2O_3$ | — | — | — | — |
| *b*. Bodies containing organic or other | — | — | — | $C_{12}H_9N_2(NH_2)$ | $C_{12}H_8N_2(NH_2)_2$ | | $C_{12}H_7N_2(NH_2)_3$ | — |
| radicals.. .. .. | — | — | — | $K_2O.CrO_3$ | — | $K_2O.(CrO_3)_2$ | — | — |

and $m'''$ their respective molecular weights, then the specific heat of the first of the series is—

$$\frac{a+b+4c}{m'},$$

and the above expression becomes—

$$\frac{(a+b+4c)\times 273\times m'}{m'} = (a+b+4c)273$$

and so for the rest, substituting $m''$ and $m'''$ for $m'$.

Whence it appears that if all these bodies were white at the absolute zero, then to give them their respective colours at the normal temperature equal amounts of heat have been expended on molecular weights of them. Or if we compare equal weights of such a series of bodies, then the greater the change of colour effected through the given range of temperature, and the less the amount of heat expended, *i.e.*, the calories used up in changing equal weights bear an inverse relation to the molecular weights, being with every probability their reciprocals, viz., $\frac{1}{m'}$, $\frac{1}{m''}$, and $\frac{1}{m'''}$.

The idea here introduced of universal whiteness at absolute zero brings us round to the case of white bodies at the normal temperature. At higher temperatures they may change, and if they do one may safely predict that it will be in accordance with the law of colour, *i.e.*, in the race of colour change the bodies of higher molecular weight will get nearer to the black end of the scale than those of lower molecular weight comparable with them. This is illustrated by the oxides of magnesium and zinc, which are both white at normal temperatures, but at a temperature below red heat the ZnO has become yellow and the MgO still remains white by contrast.

In conclusion of this paper I would add a word regarding the law of colour and constitution enunciated in my first communication to meet objections which have been raised against it. The Table above may be taken as types of the comparable bodies which conform to it.

Out of 508 examples of bodies studied the exceptions to the law of colour amount to about 6 per cent, and of these exceptions the largest number come under the third division.

Halifax, Jan. 30, 1893.

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# THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.

By GERHARD KRÜSS.

A SOLUTION of the earthy chlorides behaves on electrolysis like the solution of a hydroxide in dilute hydrochloric acid. $(Cl)_2$ and $(H)_2$ are evolved at the electrodes, the solution of the earthy chloride loses more hydrochloric acid, and allows hydroxide to deposit in an increasing quantity in proportion to the decrease of the solvent.

In this manner varying quantities of earths can be eliminated from the chloride solutions of mixtures of the rare earths, when it is to be expected that those bases which prove weakest in contact with hydrochloric acid are first thrown down as hydroxides as soon as a part of the hydrochlorides are decomposed by electrolysis. The stronger bases remain still in solution as mere stable chlorides. In order to withdraw the hydrochloric acid from a chloride solution of rare earths as uniformly as possible in all parts of the liquid, electrodes with large surfaces were applied. (This is requisite to prevent the proportion of hydrochloric acid from becoming unequal in different parts of the liquid, when consequently feeble and strong bases of the series of the rare earths are simultaneously deposited from different parts of the solution). The arrangement of the experiment was as follows:—

The solution of the earthy chloride, as neutral as possible,* containing about 3 grms. of earth in 200 c.c. solution, was put in a beaker of 15 c.m. in diameter. The negative electrode was extended along the internal circumference of the beaker; it consisted of a net of copper wire in the shape of a cylinder jacket, and extended from the bottom of the vessel to the surface of the liquid. As a positive pole there was used the carbon of a Bunsen element placed in the axis of the beaker, and kept from contact with the negative pole by means of glass rods. The current was supplied by four Bunsen elements arranged in series, the zinc pole of one connected with the carbon pole of the following element. The liquid became heated to 40° and in ten minutes 0·4 grm. of the earth were deposited as a heavy, dense precipitate. The appearance of this deposit is quite different from that of the light, bulky matter obtained on precipitating the chloride solutions of the rare earths with ammonia. The first separation obtained by electrolysis was filtered off, the filtrate was then again exposed to the current for ten minutes in the same manner as before, and so a second, third, &c., fraction of hydroxide was separated from the mixture of the earths. In order to show the *modus operandi* of this procedure, we communicate an experiment in which an yttria-earth dissolved as chloride was submitted to electrolysis.

The yttria employed was analysed. From the result of the determination of the equivalent there was calculated: $\overset{\text{III}}{R}=97{\cdot}1$ for the earth in question. It was the second member of a series of fractions in which a large quantity of yttria earth was decomposed by precipitating the chloride with aniline in an alcoholic solution:—

| Precipitation 1. | Precipitation 2. | Precipitation 3. |
|---|---|---|
| $\overset{\text{III}}{R}=99{\cdot}58$ | $\overset{\text{III}}{R}=97{\cdot}7$ | $\overset{\text{III}}{R}=102{\cdot}5$ |

By aniline as well as by ammonia there are thrown down in the first precipitation in general a more feebly basic oxide than in the second, and in the third more powerful bases than in the second precipitation. Constituents both of the first and of the third precipitation† must also be present in the second precipitation according to the general behaviour of the rare earths. On the further elaboration of the latter, according to a method which re-arranges the constituents of this fraction (No. 2), according to their basicity, a similar series of fractions will result from the precipitation No. 2, as it is shown by the above fractions in Fig. 1.

The impure yttria (precipitation No. 2, $\overset{\text{III}}{R}=97{\cdot}7$), was

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* Neutrality is obtained by evaporation on the water-bath.

† $\overset{\text{III}}{R}$ of fraction 1, as of fraction 3, is in the above case $>\overset{\text{III}}{R}$ than fraction 2.

now submitted to electrolysis as a chloride solution, and resolved into five fractions by the partial separation of hydroxide. For the separation of each of the five precipitates ten minutes were required. After determining the combining weight of the earths the following mean values are calculated for $\overset{\text{III}}{R}$ in the several fractions.

*Separations by Electrolysis.*

| No. 1. | No. 2. | No. 3. | No. 4. | Residue. |
|---|---|---|---|---|
| 107·39 | 93·5 | 105·23 | 107·7 | 137·31 |

This curve quite answers the expectations which might be entertained concerning the decomposition of the material $\overset{\text{III}}{R} = 97{\cdot}1$ of No. 1. Both branches of the curve to the right and the left ascend more suddenly from the minimum ($\overset{\text{III}}{R} = 93{\cdot}5$) of No. 1.

Hence, the electrolysis of the solutions of the rare earths seems a suitable method of working up the earths. The examination of this subject is being continued. The above experiments were conducted by the author's assistant, Dr. Karl Hofmann.—*Zeit. fur Anorgan. Chemie*, vol. iii.

## ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

In the Chemical News, vol. lxvii., p. 1, Dr. Gladstone makes some criticisms on a paper of mine of the above title, which appeared in the Chemical News, vol. lxvi., p. 177. In the first place, I must apologise for having been so careless as to miss noticing his account of experiments on the effect of adding water to solutions of ferric sulphocyanate, and also for partly misunderstanding the point of view from which his experiments were made. At the same time, I do not understand why, having noticed the effect of water, Dr. Gladstone persisted in his method of colour comparison of the various solutions. In this method one solution was diluted with water till when viewed horizontally in a test-glass it appeared of the same tint as the standard solution, the total volume of the liquid being taken as a measure of the amount of ferric sulphocyanate present in the solution. As the addition of water was known to cause a decrease in colour effect, the amount added surely could not be taken as a measure of the additional ferric sulphocyanate formed, and it is not remarkable that, as Dr. Gladstone himself found, the results obtained were not expressible in the form of an equation.

Dr. Gladstone quite correctly states that my results are never in direct contradiction to his, but he blames me for the very theoretical conclusions I have drawn from them. I do not think, however, that any other conclusions can be drawn from the experiments on the colour values of solutions of potassium sulphocyanate and varying quantities of ferric chloride at various dilutions, than that the effect of adding ferric chloride is twofold, viz., that it causes an increase of colour by rendering the ferric sulphocyanate molecules present more stable and less dissociated, and that it causes a decrease of colour by actually dissolving or in some way decomposing some of these molecules. How else can the colour values calculated for infinite concentration be accounted for? The actual reactions of salts such as ferric chloride and potassium sulphocyanate are unsuitable for directly demonstrating the law of mass, for potash has so very much greater an affinity for hydrochloric acid than for sulphocyanic acid, and also is so very much stronger a base than ferric oxide, that practically, to within 98 per cent or more, there are only present potassium chloride and ferric sulphocyanate in a solution of equivalents of these salts at infinite concentration. This conclusion was of course impossible to prove experimentally, the experiment with barium sulphocyanate and ferric sulphate merely showing that the removal of the other reacting salt from the solution produced practically no increase of colour.

With regard to the changes of colour on heating ferric sulphocyanate solutions, Dr. Gladstone mentions that he has noticed that ferric chloride solutions themselves greatly increase in colour on heating, and he considers that this has led me astray in my explanation of the results. In the Chemical News, vol. lxvi., p. 141, I myself have given numerical values for the effect of heating moderately concentrated ferric chloride solutions. These results show that the change of colour is considerable, and also that it is greater the more dilute the solutions, as Dr. Gladstone himself found. Only a small part of the change on heating the ferric sulphocyanate solutions is due to the ferric chloride, however, for, as Dr. Gladstone has shown, the addition of one equivalent of potassium sulphocyanate to 100 equivalents of ferric chloride increases the colour effect twentyfold. The results on p. 214 prove that my explanation was correct. Thus, on heating solutions of one equivalent of potassium sulphocyanate and 100 equivalents of ferric chloride, at a dilution of 160 litres, from 20° to 60°, the colour effect increases 41 per cent. On heating a solution containing the same number of equivalents, only diluted to 800 litres, the increase of colour effect at 60° is only 18 per cent. In this solution, therefore, though the ferric chloride must have caused a considerably greater effect than in the more concentrated solution, the increase of colour on heating is less than half. I think, therefore, that it must be concluded that ferric sulphocyanate solutions under suitable conditions increase in colour effect on heating, according to the general rule found to obtain for other salt solutions by Dr. Gladstone (*Phil. Mag.*, 1857) and independently by myself (Chemical News, vol. lxvi., p. 141).

In conclusion, I must thank Dr. Gladstone for criticising my paper in so kindly a spirit. I hope my experiments and remarks may be taken rather as a continuation of his experiments, which at the time they were published had such an important effect on the progress of chemical inquiry, than as a hostile criticism of them.

## MANURIAL EXPERIMENTS WITH TURNIPS.*

By C. M. AIKMAN, M.A., B.Sc., F.R.S.E.,
Lecturer on Agricultural Chemistry, Glasgow and West of Scotland Technical College, and Glasgow University Extension Board.

(Continued from p. 59).

The turnips were lifted in the beginning of December, and weighed as follows:—

| No. | Manure. | Produce. | | | Increase over nothing plots. | | |
|---|---|---|---|---|---|---|---|
| | | T. | cwt. | qr. | T. | cwt. | qr |
| 1. | Nothing .. .. .. .. .. | 3 | 8 | 3 | — | | |
| 2. | 4 cwt. super .. .. .. .. | 19 | 0 | 0 | 10 | 17 | 3 |
| 3. | 8 cwt. super .. .. .. .. | 19 | 15 | 0 | 11 | 12 | 3 |
| 4. | 6 cwt. slag .. .. .. .. | 17 | 1 | 1 | 8 | 19 | 0 |
| 5. | 12 cwt. slag .. .. .. .. | 17 | 16 | 1 | 9 | 14 | 0 |
| 6. | Nothing .. .. .. .. .. | 12 | 15 | 3 | — | | |
| 7. | 6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda .. | 28 | 0 | 0 | 19 | 17 | 3 |
| 8. | 6 cwt. slag and 15 tons dung | 24 | 12 | 2 | 16 | 10 | 1 |
| 9. | 12 cwt. slag and 15 tons dung | 25 | 18 | 3 | 17 | 16 | 2 |
| 10. | 12 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda .. | 28 | 2 | 2 | 20 | 0 | 1 |

No. 11 was not weighed, as Mr. Graham considered it valueless as a nothing plot, as it received slag blown over from No. 10.

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* From the *Transactions of the Highland and Agricultural Society of Scotland.*

In calculating the nothing plots I have taken the mean of plots Nos. 1 and 6. Plot 6 received a little slag from No. 5; and that, Mr. Graham thinks, will account for the difference. With regard to No. 1, I wrote Mr. Graham on receiving his results, asking him if he was quite convinced of their accuracy, and received the following reply: "The statement I have given in regard to No. 1 (nothing plot) is thoroughly correct. There was no circumstance connected with it in any way calculated in the least to give it an unfair chance. Every plant lived on till the time for storing, but they were useless dwarfs."

It will be seen from the above results that the plots which show the biggest returns are Nos. 7 and 10—those which received slag, dung, and nitrate of soda. There is very little difference between the two. Nos. 8 and 9 come next—those which received slag and dung; No. 9, which received the larger quantity of slag, giving about 1½ tons more turnips than No. 8. Between plots Nos. 2 and 3—viz., those which received "super" alone in greater and smaller quantity respectively—there is not much difference, only some 15 cwt., not sufficient to justify the additional expense of the larger quantity of super.

The plots which show the lowest returns are those which received slag alone. Whether, however, this shows slag to be inferior in worth as a manure in this case to super cannot be inferred until we compare the cost of the manures. This, accordingly, will be seen from the following table:—

| No. | Manure. | Cost. | Value of increase in crop. |
|---|---|---|---|
| 2. | 4 cwt. super.. .. .. | £0 11 0 | £4 6 0 |
| 3. | 8 cwt. super.. .. .. | 1 2 0 | 4 13 0 |
| 4. | 6 cwt. slag .. .. .. | 0 6 0 | 3 11 6 |
| 5. | 12 cwt. slag .. .. .. | 0 12 0 | 3 17 6 |
| 7. | 6 cwt. slag, 15 tons dung, and 1 cwt. nitrate of soda .. | 5 6 0 | 7 19 0 |
| 8. | 6 cwt. slag and 15 tons dung .. .. .. | 4 16 0 | 6 12 0 |
| 9. | 12 cwt. slag and 15 tons dung .. .. .. | 5 2 0 | 7 2 8 |
| 10. | 12 cwt. slay, 15 tons dung, and 1 cwt. nitrate of soda .. | 5 12 0 | 8 0 0 |

(*N.B.* The turnips were sold at 8s. per ton).

An examination of the above table will show that in every case there is a fair margin of profit, the most profitable being Nos. 2, 3, 4, and 5, those which received mineral manure alone. Of these No. 2 shows best—that which received 4 cwt. super per acre—a profit of £3 15s. No. 3 comes next, showing a profit of £3 11s.; while Nos. 4 and 5 are exactly the same. In this case, then, it may be said that the slag is weight for weight one half as valuable as the super. As, however, the slag contains only a little more than half the percentage of phosphates, the unitary value of the phosphates in each is practically the same.

In these experiments, as in the previous series, the dung does not justify its application. By comparing the results of plots Nos. 4 and 8 it will be seen that the addition of 15 tons of farmyard manure, costing £4 10s., only gave an increase of 7½ tons, possessing the value of £3, while comparison between Nos. 5 and 10 will show a similar result.

Comparing plots Nos. 7 and 8, and 9 and 10, it will be found that, in the first case, 1 cwt. of nitrate of soda, costing 10s., was the means of increasing the crop to the extent of over 3 tons, value £1 7s.; while in the second, the increase amounted to only about 2 tons, value 17s.—sufficient, however, to show a profit.

The next series of experiments about to be described were those carried out by Mr. A. Stevenson, at his farm of Parkhill, Tarbolton, Ayrshire. The soil of the field experimented upon was a sandy loam, naturally not fertile, but which had been liberally treated for many years, and yielded fair crops. The mechanical and chemical analysis of the soil is as follows:—

(*a*) Mechanical analysis—

| | |
|---|---|
| Clay .. .. .. .. .. | 52·41 per cent |
| Sand .. .. .. .. .. | 47·59 ,, |
| | 100·00 |

(*b*) Chemical analysis (soil dried at 212° F.)—

| | |
|---|---|
| Organic matter (containing nitrogen, 0·207) .. .. .. .. | 7·770 |
| Iron sesquioxide and alumina .. | 3·900 |
| Lime .. .. .. .. .. .. .. .. | 0·616 |
| Magnesia .. .. .. .. .. .. .. | 0·200 |
| Potash .. .. .. .. .. .. .. | 0·173 |
| Soda .. .. .. .. .. .. .. .. | 0·154 |
| Sulphuric acid .. .. .. .. .. | 0·073 |
| Phosphoric acid .. .. .. .. .. | 0·207 |
| Insoluble siliceous matter, chlorine, carbonic acid, &c. .. .. .. | 86 907 |
| | 100·000 |

Mr. Stevenson describes its past history as follows:—"In 1883 the field was ploughed out of lea, and a crop of oats taken. The oats received 1½ cwt. super, 1 cwt. dissolved bones, and 1 cwt. nitrate of soda per acre. In 1884 there was a crop of potatoes, which were manured with 18 tons farmyard manure, 2 cwt. super, 2 cwt. dissolved bones, and 1 cwt. sulphate of ammonia per acre. In 1886 there was a crop of hay, which was manured with 1 cwt. super, 1 cwt. dissolved bones, and ½ cwt. sulphate of ammonia per acre. In 1887 a crop of hay was grown, which received the same quantity of manure as was applied the previous year; and in 1888 a crop of oats was grown, which received the same manures as those applied in 1883."

The ground is low-lying, and has a southern as well as a northern exposure. The plots were ten in number, each being 1-10th of an acre in extent.

The following is a statement of the different plots, with the quantities of manures each received and the produce yielded:—

| No. | Manure. | Produce. Tons. | Produce. cwt. | Increase over nothing plots. Tons. | Increase over nothing plots. cwt. |
|---|---|---|---|---|---|
| 1. | Nothing .. .. .. .. .. | 16 | 12 | — | — |
| 2. | 6 cwt. slag .. .. .. | 19 | 0 | 2 | 8 |
| 3. | 4 cwt. super .. .. .. | 20 | 17 | 4 | 5 |
| 4. | 12 cwt. slag .. .. .. | 23 | 12 | 7 | 0 |
| 5. | 8 cwt. super .. .. .. | 23 | 0 | 6 | 8 |
| 6. | 12 cwt. slag and 20 tons dung .. .. .. .. | 28 | 7 | 11 | 15 |
| 7. | 12 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda .. .. .. .. .. | 31 | 0 | 14 | 8 |
| 8. | 6 cwt. slag and 20 tons dung .. .. .. .. | 26 | 15 | 9 | 3 |
| 9. | 6 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda .. .. .. .. .. | 30 | 10 | 13 | 18 |
| 10. | 5 cwt. super and 20 tons dung .. .. .. .. | 33 | 0 | 16 | 8 |

The largest returns are obtained from plot No. 10—that receiving 5 cwt. super and 20 tons dung—viz., 33 tons per acre, or 16 tons 8 cwt. of an increase over the average of the nothing plots.

The following table shows the value of the manures and the value of the increase of crop produced by them. The most profitable plot, it will be seen, is No. 4, which received slag alone at the rate of 12 cwt. per acre. Again it will be seen that, with the exception of plot No. 10, farmyard manure applied did not give its value in increase of crop.

| No. | Manure. | Cost. | Value of increase in crop. |
|---|---|---|---|
| 2. | 6 cwt. slag .. .. .. | £0 6 0 | £1 9 0 |
| 3. | 4 cwt. super.. .. .. | 0 11 0 | 2 11 0 |
| 4. | 12 cwt. slag .. .. .. | 0 12 0 | 4 4 0 |
| 5. | 8 cwt. super.. .. .. | 1 2 0 | 3 17 0 |
| 6. | 12 cwt. slag and 20 tons dung . .. .. .. | 6 12 0 | 7 1 0 |
| 7. | 12 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda .. | 7 2 0 | 8 13 0 |
| 8. | 6 cwt. slag and 20 tons dung . .. .. .. | 6 6 0 | 5 10 0 |
| 9. | 6 cwt. slag, 20 tons dung, and 1 cwt. nitrate of soda .. | 6 16 0 | 8 1 0 |
| 10. | 5 cwt. super and 20 tons dung . .. .. .. | 6 13 9 | 9 17 0 |

A comparison of plots Nos. 2 and 3, and Nos. 4 and 5, will show that in the first case super shows better than the slag, while in the second case slag shows better than the super. Again, in both cases where the nitrate of soda has been used it shows a very marked increase. Thus in plot No. 7, 1 cwt. of nitrate of soda (costing 10s.) has given an increase of crop over plot No. 6 of the value of £1 12s., while in plot No. 9 the increase over plot No. 8 is £2 11s.

(To be continued).

ON THE

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E., and J. B. HENDERSON.

(Continued from p. 56).

### *Dumas's Research Critically Considered.*

DUMAS's method, or rather that of Berzelius (because it was he who invented it, as every student of chemistry is aware), consists in this, that a given quantity of oxide of copper is reduced in hydrogen gas, and the loss of weight suffered, that is to say, the oxygen given up by the oxide compared with the weight of water produced. This is no occasion for describing the exact *modus operandi* which was adopted by Berzelius, but we must name the refinements upon it which were introduced by Dumas. One of these was that he worked on a far larger scale than his predecessor had done, and another, that he took care to purify and dry his hydrogen more fully by passing it through long successive columns of (1) solution of nitrate of lead, (2) solution of nitrate of silver, and (3) pumice soaked in oil of vitriol or powdered over with phosphoric anhydride. Dumas, besides, took special care to not allow the surplus hydrogen and the air which he passed through the water receptacle at the end of an experiment to escape without having first been most thoroughly dehydrated by means of tared tubes containing one or the other of the two dehydrators named.

But the principal improvement by Dumas was that he evacuated his reduction tube, both before and after the experiment, before taking it to the balance. The difference of the two weighings thus gave the *true* weight of the oxygen quite directly, and the errors, which would otherwise have been caused by the gases condensed in the pores of the oxide and of the metal, were eliminated at the same stroke. The water produced was weighed in the ordinary way—we mean "not *in vacuo*." Referring to Dumas's memoir for more detailed information on his mode of working, we will now pass to a review of his results, as tabulated by him on page 200 of his memoir. A superficial examination of this table sufficed to show that it is not free from misprints. To detect these we recalculated all his "*equivalents bruts*," and in doing so had no difficulty in spotting and rectifying the errors. The results of our calculations are included in the following Table:—

| Number. | | $n$. | $k$. | $k-k_0$. | Order of residuals. |
|---|---|---|---|---|---|
| 3 .. | .. | 20 | 1·12481 | −0·00066 | 19 |
| 19 .. | .. | 31 | 1·12488 | −0·00059 | 18 |
| 2 .. | .. | 20 | 1·12490 | −0·00057 | 17 |
| 8 .. | .. | 46 | 1·12500 | −0·00047 | 16 |
| 10 .. | .. | 52 | 1·12504 | −0·00043 | 15 |
| 1 .. | .. | 13 | 1·12505 | −0·00042 | 14 |
| 4 .. | .. | 57 | 2·12506 | −0·00041 | 13 |
| 16 .. | .. | 37 | 1·12506 | −0·00041 | 12 |
| 11 .. | .. | 52 | 1·12512 | −0·00035 | 10 |
| 12 .. | .. | 60 | 1·12533 | −0·00014 | 3 |
| 7 .. | .. | 35 | 1·12546 | −0·00001 | 1 |
| 15 .. | .. | 56 | 1·12558 | +0·00011 | 2 |
| 5 .. | .. | 76 | 1·12566 | +0·00019 | 4 |
| 6 .. | .. | 44 | 1·12568 | +0·00021 | 5 |
| 17 .. | .. | 34 | 1·12575 | +0·00028 | 6 |
| 13 .. | .. | 62 | 1·12577 | +0·00030 | 7 |
| 18 .. | .. | 32 | 1·12580 | +0·00033 | 8 |
| 14 .. | .. | 52 | 1·12581 | +0 00034 | 9 |
| 9 .. | .. | 60 | 1·12585 | +0·00041 | 11 |

Column 1 gives the order in which the several experiments are enumerated on Dumas's table; col. 2, under "$n$," the weights of oxygen operated upon, rounded off to the nearest integer number of grms.; col. 3, for each experiment, the weight of water obtained per grm. of oxygen, as "$k$." In the heading to col. 4 the symbol $k_0$ stands for the most probable value of the ratio $H_2O:O$ calculated by us; the numbers in col. 5 arrange the values $k-k_0$ in the order of their magnitude, irrespective of their signs.

For any one of the nineteen syntheses we have an equation of the form $W-Sk_0=\delta$, where S stands for the (exact) weight of oxygen and W for the weight of water found, and $\delta$ for the error in the water-weight found, supposing $k_0$ to be the true value of $H_2O:O$. We brought the equation into the form $S(k-k_0)=\delta$ (which was more convenient to us, because we had already calculated the values $k$), and then, substituting for every S its corresponding $n$, calculated that value for $k_0$, which, supposing it to be substituted in all the equations, would reduce the sum of the squares of the values $\delta$ to its minimum. The result was $k_0=1·12547$. From the list of errors in the last column we calculate that the "probable" error of a single determination is $r=\pm 0·000303$, which, indeed, is not far removed from the tenth of the values $k-k_0$; for the probable error of the mean we find $r_0=\pm 0·000070$. In all that we have stated the word "error," of course, means that part of the total error which is owing to accidental causes, and even in this sense $r_0$ does not represent more than a fraction of the uncertainty. For a guess the latter may be put down at three times the probable error; if we do so our calculation shows that, supposing Dumas's determinations were free of method errors, the true value of $k$ could be said to lie between 2·1253 and 1·1257.

In the present case the accidental part of the error of any one result may be taken as being a function of the errors of the four weighings involved. Assuming, for an approximation, that the probable values of these four errors were all of the same magnitude $\pm x$, we have for the probable error in the water-weight, W, and for that in the oxygen-weight, S, the same value, $x\sqrt{2}$, and for the relative probable errors in W, and in S or $\frac{1}{S}$, the expressions $\frac{x\sqrt{2}}{W_0}$ and $\frac{x\sqrt{2}}{S_0}$, respectively. Hence we may write—

$$W\times\frac{1}{S}=\left(W_0\pm\frac{x\sqrt{2}}{W_0}\,W_0\right)\times\left(\frac{1}{S_0}+\frac{x\sqrt{2}}{S_0}\cdot\frac{1}{S_0}\right)$$

---

* *Proceedings of the Philosophical Society of Glasgow.*

Hence, according to a rule of the method of the last squares, if $r$ be the probable error of the product,

$$r^2 = \frac{W_0{}^2}{S_0{}^2} \cdot \frac{2x^2}{S_0{}^2} + \frac{1}{S_0{}^2} \cdot 2x^2.$$

Hence, as $\frac{W}{S} = 1{\cdot}125$ very nearly,

$$r = \pm 2{\cdot}129 \frac{x}{S_0}.$$

Dumas's average value for S was about 44 grms.; hence we have for what one might call his average "experiment,"—

$$x = \pm 6{\cdot}2 \text{ m.grms.}$$

In other words, the value 0·0003 recorded above for the probable error of a single experiment may be explained by assuming that the probable error of each of his four weighings was = ± 6 m.grm., and that the real error varied from something like − 18 to something like + 18 m.grm.; and this is a fair enough guess, considering that the apparatus he used were uncommonly heavy and bulky. His reduction tube, for instance, cannot have displaced much less than 600 m.grms. of air, and supposing the density of the air to have changed between the two weighings by 1/30 of its value, this alone would make his oxygen-weight wrong by ± 20 m.grms. To pass to "Dumas's Method Errors," the most obvious of these is the one caused by the unavoidable presence of atmospheric air in even the most carefully prepared hydrogen gas. As already stated in the prefatory note, Dumas sought to eliminate this error by calculating for each of his syntheses the weight of water produced from the atmospheric oxygen introduced as part of the sulphuric acid used for the making of the hydrogen, and deducting the result from the total weight of water as found by direct weighing. His mean "*equivalent corrigé*" is by 0·00018 less than his corrected mean. Deducting this from our $k = 1{\cdot}12547$, we have for the corrected number 1·12529, or, for O = 16, H = 1·00232. Unfortunately, however, Dumas does not tell us how he procured the data for his correction; and, besides, if we consider that his hydrogen had to travel through some seven metres of U-tubes, charged, some of them, with porous materials, before it reached its destination, it is impossible not to suspect that his gas contained other adventitious oxygen, besides that derived from the dilute sulphuric acid which went into the gas-evolution bottle. Under these circumstances we thought we had better try and determine Dumas's adventitious oxygen as far as now possible ourselves, and we thus came to carry out the experiment referred to in the prefatory note as having given us the conviction that his correction was below the truth. This experiment (detailed hereafter as Exp. I.) was, of course, meant to be repeated, and it really was, but only after the intervention of a deal of other work. At the time it struck us that being, unlike Dumas, in possession of a method for the production of a current of absolutely oxygen-free hydrogen, the best thing we could do was to effect a series of quantitative syntheses of water by means of such gas, provided only we took care to maintain our critical attitude, and to do to our own work what we had originally proposed to do in reference to that of our great predecessor. As an important preliminary, we tried to ascertain whether it is possible to pass a current of hydrogen over a surface of red-hot glass without producing at least traces of water from it and the oxygen of the bases in the outer skin of the tube.

For this purpose we carried out two series of experiments. In the first we passed the gas over relatively large surfaces of red-hot glass, and weighed the water produced from a known volume of hydrogen. In the second experiment we aimed more directly at the probable magnitude of supposed error by carrying out a number of quantitative syntheses of water with, in general, large known volumes of hydrogen, but varying weights of oxide of copper. Supposing S to stand for the weight of oxygen used up in a given synthesis, W for the weight of water produced, and V for the number of litres of hydrogen which passed through the hot reduction tube over and above the minimum which would have sufficed to convert those S grms. of oxygen into water, we have $W = kS + k'V$, and theoretically all that is required for the determination of the constants are two syntheses—one carried out with little, and the other with a large excess of hydrogen gas. But in practice it is better to determine the first constant $k$ (which obviously, if we weigh in air, is not the true value of $H_2O : O$) by means of a few experiments with relatively large quantities of oxide of copper and small excesses of hydrogen, and then to substitute this $k$ in the calculation of syntheses made with small quantities of the oxide to find $k'$. We, however, commenced with these latter determinations, and, in their original interpretation, assumed that $k$ was equal to 1·125 exactly, which in a practical sense was confirmed by the syntheses subsequently carried out with large weights of oxide of copper. These syntheses were quite completed and calculated when we made a very unwelcome discovery. To prepare for the (it does not matter now what) experiment, we had filled a Dumas system of hydrogen purifiers with the gas by means of a Kipp, closed the outlet, and left the apparatus in this condition over night. When we turned on the hydrogen on the following morning, the gas was found to smell so strongly of sulphurous acid that it would have been impossible not to notice it. We had made quite sure of the absence of this impurity from our vitrioled pumice; hence it was clear that it had been produced from the sulphuric acid by its prolonged contact with hydrogen. But Dumas's syntheses, as we are informed, always took some ten hours for their execution; hence his hydrogen must have been contaminated with sulphurous acid in all those cases at least in which he dehydrated it by means of oil of vitriol. We accordingly instituted a comparison of the results of these experiment with those which he arrived at when he dehydrated his gas with phosphoric anhydride, but we could not see any marked difference, and concluded that he used the more powerful dehydrator, not by itself, but as an auxiliary to oil of vitriol. But, be this as it may, our own syntheses, although they were carried through in far less time, and although our vitrioled pumice tubes were far smaller than Dumas's, must in some measure have been effected by the same error. It was also clear that what had so far been put down by us as "adventitious oxygen $O_2$," had partly consisted of $SO_2$. We therefore made a series of critical experiments to determine the magnitude of the corresponding error, and, in our final series of syntheses, used fused caustic potash combined with phosphoric anhydride as sole dehydrators. After this digression we will now proceed to give a brief but sufficiently detailed account of all those of our experiments which bear more directly on the question under discussion.

### I.—*Determination of the Adventitious Oxygen in Dumas's Hydrogen.*

*Experiment* I.—The apparatus used consisted of the following successive parts:—

1. A "Kipp," or a combination of two Kipps (*vide infra*), charged with ordinary (we mean unboiled) dilute sulphuric acid.
2. A close imitation of Dumas's set of purifying tubes for the hydrogen, namely:—
    - (*a*) A tube charged with glass fragments and a strong solution of nitrate of lead.
    - (*b*) A similar tube with solution of sulphate of silver. In these two tubes the volume of reagent was so adjusted that the gas had to bubble through a not inconsiderable column of liquid in the bent portion.
    - (*c*) A third tube, of which the entrance limb was charged with fragments of pumice which had

been boiled with solution of caustic potash, and the other with fragments of the fused reagent.

(*d and e*) Two tubes charged with fragments of fused caustic potash.

(*f and f'*) Two tubes charged with fragments of pumice soaked in oil of vitriol.*

The only deviation from Dumas's design which we allowed ourselves consisted in this, that not having such very large U-tubes as he used at hand, we gave our tubes the form of rather flat V's, as shown by Fig. 2.

Our tubes, however, had the same length as Dumas's, so that the gas, as in his case, had to travel through about seven metres of purifying tubes on its journey.

3. A tared "witness tube," G, charged with vitrioled pumice.

4. A combustion tube, 370 m.m. long, and 15 m.m. wide inside, charged with as thick a closely wound spiral of fine copper gauze as it would hold, and then drawn out at both ends to avoid the use of corks or indiarubber stoppers.

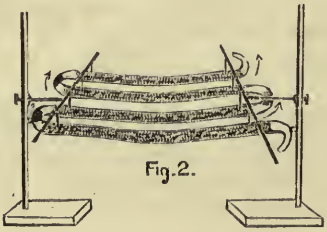
Fig.2.

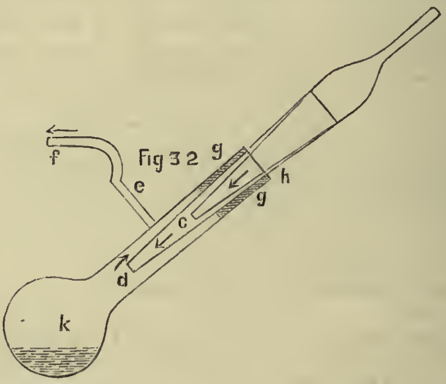
Fig 3 2

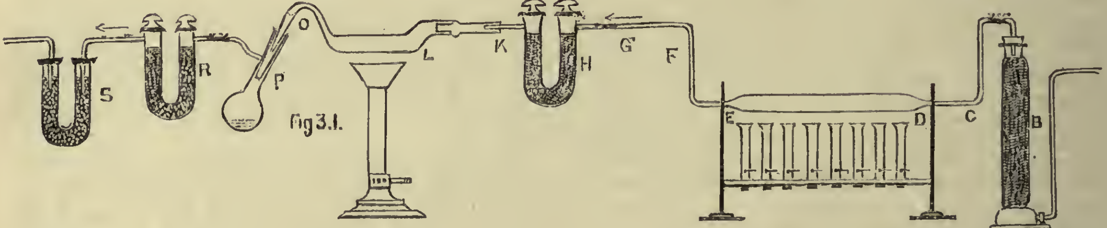
Fig 3.1.

5 and 6. Two U-tubes charged with vitrioled pumice; the first, K, was tared; the second, L, not; because it served only as a protection tube against ingress of vapour of water from the atmosphere, or from No. 7, which was a large graduated "Pisani bottle," in which the outgoing gas was collected and measured.

The following shows the sequence of the apparatus :—

| Kipp. | Dumas's purifiers. | U-tube. vitriol. | Combustion tube. | U-tube vitriol. | U-tube vitriol. | Pisani. |
|---|---|---|---|---|---|---|
| (1) | *a,b,c,d,e,f,f'* | G | Red hot copper. | K | L | (7) |

In the actual experiment, the first step was to pass hydrogen through the Dumas purifiers until the gas would have been deemed free of air for any ordinary purpose. The weighed witness tube, G, and the copper-gauze tube were then attached, and after the copper had become red hot, three further litres of hydrogen were sent through the apparatus to purge the copper from its water and oxygen. This being done, the weighed tube, K, and its protection tube were attached, and the experiment continued until a sufficiency of hydrogen had accumulated in the Pisani. At the end, the tubes K and L were detached, the hydrogen in the former displaced by vitriol-dried air, and this tube weighed—the flames under the copper gauze tube being turned off immediately after the removal of K. As soon as the copper tube had cooled down sufficiently, the witness tube, G, was detached and got ready for the balance. The volume of hydrogen operated upon amounted to 12 litres, which passed through in 3·5 hours. Tube G gained 0·2 m.grm.; tube K, 3·45 m.grm., or 0·288 m.grm. per litre of hydrogen used.

*Experiment* II.—(Done long after I.). The apparatus used differed from that used in I. only in this, that in place of the copper-gauze tube we inserted the reduction tube of our apparatus for the quantitative syntheses (L O in Fig. 3) full of reduced copper as it came from one of these. The volume of hydrogen operated upon was ten litres, and the weight of water produced from it = 7·65 m.grm., but the witness tube corresponding to G of Exp. I. gained 10·8 m.grm.

*Experiment* III.—(Done immediately after II.). In this experiment we obtained 8·2 m.grm. of water from 11 litres of hydrogen, or 0·745 m.grm. per litre. The witness tube this time gained only 0·4 m.grm.

*Experiment* IV.—(Done long after the preceding ones, and after we had come to observe the reducing action of hydrogen on oil of vitriol). The apparatus consisted of the following successive parts :—

1. A Kipp.
2. The set of Dumas purifiers up to the last caustic potash tube, designated as "(2) *d*" under Experiment I. The two vitriol tubes, *f* and *f'*, were omitted.

---

* We will avail ourselves of this opportunity for stating how we prepared our vitrioled-pumice tubes. After having made sure of the absence of nitrogen oxides and of sulphurous acid from our vitriol, a quantity of cut-up pumice was placed in a large platinum basin, covered with a large excess of the acid, and the acid then kept at a boiling heat until about one-half of it had volatilised. The whole was then allowed to cool under a bell-jar, the surplus vitriol poured off, and the "vitrioled pumice" at once transferred to its U-tubes. When a tube had to be re-charged, it was filled completely with fresh acid (previously boiled down in a platinum basin to expel more volatile impurities), allowed to stand for ten minutes, and the surplus vitriol then poured off. This washing process was repeated once, and the tube then deemed ready for use.

3. From *d* the gas passed on successively to a tared witness U-tube, K, charged with recently fused caustic potash, and followed by a tared U-tube, P, containing pumice and phosphoric anhydride, respectively (*vide infra*, under "final syntheses"); the reduction tube full of reduced metallic copper; a tared U-tube, $K_1$, and a witness U-tube, $P_1$, charged with fused caustic potash and phosphoric anhydride, respectively; a protection tube containing fused caustic potash; and, lastly, the graduated Pisani bottle.

The exact *modus operandi* needs not be described; it suffices to state the results as follows:—The volume of hydrogen operated upon was 12 litres; the tubes K and P gained 1·5 and 0·2 m.grm. respectively, the tubes, $K_1$ and $P_1$, 2·5 m.grm. and *nil*. Hence, water produced 2·5 m.grm. or 0·208 per litre of hydrogen used.

*Experiment* V.—(Followed immediately after No. 4, and was done in exactly the same manner). Increase of weight suffered by tubes K, P, $K_1$, $P_1$, = 0·7, 0·2, 2·3, 0·2 m.grm. respectively; volume of hydrogen used = 12 litres; hence, water produced per litre of hydrogen = 2·5 : 12 = 0·208.

Hence we had, for the potential water in Dumas's hydrogen, m.grms. per litre:—

| | Experiment— | | | | |
|---|---|---|---|---|---|
| | I. | II. | III. | IV. | V. |
| From $O_2$ and $SO_2$.. | 0·288 | 0·765 | 0·745 | | |
| From $O_2$ alone .. | | | | 0·208 | 0·208 |

In the case of Nos. II. and III. the gas probably was largely contaminated with sulphurous acid.

(To be continued).

## THE INSTITUTE OF CHEMISTRY.

The following letter, addressed by Prof. Thorpe to the President of the Institute of Chemistry, has been forwarded to us for publication:—

Royal College of Science,
South Kensington, S.W., Feb. 3, 1893.

Dear Mr. President,

The action of the Council of the Institute of Chemistry with respect to the Chemical Society, in their decision at the last meeting, is, in my judgment, so significant of what may now be considered the official relations of the Institute towards the sister Society, that I am compelled to tender my resignation as a member of the Council, and at the same time to withdraw from the Institute.

The mover of the resolution to omit the letters F.C.S. from the Register of the Institute, based his argument ostensibly on the assumption that Fellowship of the Chemical Society is not to be regarded as a "professional qualification." Although this resolution was subsequently amended as follows: "That in future all letters indicating membership of any society, except the Royal Society (London), be omitted in the Register from all names of members of the Institute," it will be obvious to anyone who turns to the present Register that the amended resolution, which was adopted by the Council, is practically directed against the Fellows of the Chemical Society.

The Council must know that it has no power to compel any of the members of the Chemical Society to omit the letters F.C.S. after their names if they are minded to use them: not even if the use of such letters should be construed as a "breach of decorum" in the revised code of professional ethics which the Council is about to elaborate.

It is, I am informed, very questionable whether, if a Fellow of the Institute, who is at the same time a Fellow of the Chemical Society, required that he should be designated in your Register as a Fellow of the Chemical Society by the letters F.C.S., which by use and wont are understood to indicate such Fellowship, the Council could prevent it.

There is no greater inherent value or property in the letters F.I.C. than in those of F.C.S. Whatever value may be associated with those letters is a matter of individual appraisement, depending upon the estimation by the valuer of the worth and dignity of the particular Society.

I am, of course, ready to admit that the majority of the present Council of the Institute are not actuated by unfriendly feelings towards a Society which they recognise has for more than half a century, by its publications, its research fund, and its library, fostered to the best of its power the study of Chemical Science in this kingdom; what I regret is that in following the initiative of a section which has hitherto shown itself more ready to interfere in the proceedings of the Chemical Society than to contribute to its transactions, they should have put themselves officially in an attitude of antagonism to the Chemical Society, and by seeking to interfere with the individual freedom of their members in a matter which not even the code of professional ethics could rightly take cognisance of, they should have assumed a position from which they might be compelled to retreat.

Yours very truly,
T. E. Thorpe.

Prof. Tilden, D.Sc., F.R.S.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*Ordinary Meeting, January 27th, 1893.*

Walter Baily, M.A., Vice-President, in the Chair.

Mr. T. W. Morton was elected a member of the Society.

Prof. S. P. Thompson, F.R.S., made a communication on "*Japanese Magic Mirrors*," and exhibited numerous specimens showing the magic properties. Referring to the theory of the subject, he said the one now generally accepted was that proved by Professors Ayrton and Perry in 1878, who showed that the patterns seen on the screen were due to differences in curvature of the surface. The experiments he now brought forward fully confirmed their views.

Brewster had maintained that the effects were due to differences of texture in the surfaces causing differences in absorption or polarisation, but the fact that the character of the reflected image depended on the convergency or divergency of the light and on the position of the screen, showed this view to be untenable. Another proof of the differing curvature theory was then given by covering a Japanese mirror with a card having a small hole in it. On moving the card about, the disc of light reflected from the exposed portion varied in size, showing that the curvatures of portions of the surfaces were not the same. The same fact was proved by a small spherometer, and also by reflecting the light passing through a coarse grating from the mirror, the lines being shown distorted. To put the matter to a test demanded by Brewster, he had a cast taken from a mirror by his assistant, Mr. Rousseau; this had been metallised, silvered, and polished, and now gave unmistakable evidence of the pattern reflected from the original.

The true explanation of how the inequalities of curvature were brought about during manufacture had also been given by Professors Ayrton and Perry, but there were some questions of detail on which difference of opinion might exist.

The late Prof. Govi had noticed that warming a mirror altered its possibilities. A thick mirror which gave no pattern whilst cold, but developed one on being heated, was shown to the meeting.

Professor Thompson also showed that a glass mirror having a pattern cut on the back developed magic properties when the mirror was bent. When made convex the reflected pattern was dark on a light ground, and when made concave light on a dark ground. Warming ordinary mirror glass by a heater whose surface was cut to a pattern gave similar effects. Very thick glasses could be affected in this way. On passing a spirit-lamp behind a strip of mirror, a dark band could be caused to pass along the screen illuminated by light reflected from the mirror. By writing on lead foil and pressing the foil against a glass mirror by a heater, the writing was caused to appear on the screen.

Prof. Thompson had also found that Japanese mirrors which are not magic when imported could be made so by bending them mechanically so as to make them more convex. In conclusion he showed a large mirror 15″ × 11″, the reflection from which showed the prominent parts of the pattern on its back, with the exception of two conspicuous knobs; these knobs gave no indication of their existence.

Prof. Ayrton said the simple mechanical production of the magic property described by Prof. Thompson led him to think that some experiments on "seeing by electricity" by the aid of selenium cells, which Prof. Perry and himself made some years ago, might lead to some result if repeated with thinner reflectors. Speaking of the effect of scratching the back of a Japanese mirror, he pointed out that if metal be removed by pressure a bright image was seen, whilst if removed chemically a dark image resulted. Since the original paper on the subject was written, he had been led to modify his views as to the effect of amalgamation, for some time ago he showed the Society how brass bars were bent if one edge be amalgamated, thus proving that enormous forces were developed. He now regarded amalgamation as an important part of the manufacture.

Mr. Trotter enquired if it had been proved that there was no difference in the metal in the thick and thin parts? One would expect the thin parts to be harder and polished away less.

After some remarks by Mr. J. W. Kearton and Major Rawson, Prof. Thompson said the magic effects produced by heating the back of a glass mirror remained for a short time after the heater was removed. The question of whether differences in hardness of the thick and thin parts of a mirror were of consequence in the production of the magic property had been tested by using sheets of brass thickened by pieces soldered to the back as mirrors, and found to be unimportant.

Prof. Ayrton also described an experiment pointing to the same conclusion.

Mr. W. F. Stanley read a paper on "*The Functions of the Retina.* I. *The Perception of Colour.*" Referring to Young's three-nerve theory of colour sensation, the author said Prof. Rutherford had pointed out that there was no necessity to assume that different nerves conveyed different colour sensations, for as a telephone wire would transmit almost an infinite variety of sound vibrations, so the nerves of the retina were probably equally capable of conveying all kinds of light vibrations. Prof. Rutherford had further pointed out that the image of a star could not possibly cover three-nerve terminals at once, and therefore could not be seen as white if Young's theory was correct.

The author then described Helmholtz's experiments with a small hole in a screen illuminated by spectrum colours. For red illumination the greatest distance at which the hole could be seen sharply defined was eight feet, and for violet one and a half feet. When the hole was covered with purple glass, or with red and violet glasses superposed, and a bright light placed behind, the eye, when accommodated for red light, saw a red spot with a violet halo round it, and when focussed for violet light, saw a violet spot with circle of red. These experiments, the author thinks, show that the chromatic sense in distinct vision under critical conditions (*i.e.*, where a single nerve or a small group of nerves is concerned) depends on the colours being brought to foci at different distances behind the crystalline lens. He also infers that the same focal position in the eye cannot convey simultaneously the compound impression of widely separated colours. Helmholtz's observations are further examined in the paper, and a series of zoetrope and colour disc experiments described, which tend to show that the eye cannot follow rapid changes of colour. Changes from red to violet could be followed much more quickly than from violet to red. The red impressions were, however, more permanent. The observed effects were found to depend on the intensity of the light, and also on the distance of the eye from the coloured surface.

Summing up his observations, the author infers that by systems of accommodation of the eye the colours of the spectrum are brought to focus on special parts or points of the rods or cones of the retina, such focal points being equivalent, by equal depths or distances from the crystalline lens, to a focal plane formed across the whole series of nerve terminals. That all the rays of light from one object, or part of an object, of very small area and of any spectrum colour will converge to a point upon a nerve terminal, and that this terminal will be most excited by the light.

At the end of the paper Dr. Stanley Hall's views o nerve structure are examined.

Captain Abney thought the results of the zoetrope experiments were what one would have expected when pigmentary colours were used. To be conclusive, such experiments must be conducted with pure spectrum colours. The statement about the size of star images being less than that of a nerve terminal would probably need revision. Speaking of colour vision he said the modern view was to regard light as producing chemical action in the retina, which action gave rise to the sensation of colour. On the author's theory he could not see how colour blindness could be explained.

Mr. Trotter said he understood Helmholtz to have proved that nerves could distinguish quantity, but not the quality of a stimulus. Since the speed at which stimulus travelled to the brain was about 30 metres a second, the wave length of a light vibration if transmitted in this way would be very small. Taking Lord Kelvin's estimate of the minimum size of molecules of matter, it followed that there must be many wave lengths in the length of a single molecule. This, he thought, hardly seemed possible.

Mr. Lovibond pointed out that the observations referred to by the author could be equally well explained on the supposition that six colour sensations existed. The confusion of colours he had mentioned arose from lack of light.

Mr. Stanley replied to some of the points raised by Capt. Abney.

In proposing a vote of thanks to Mr. Stanley the Chairman said it had been shown that light could be resolved into three sensations, but it was not known how this resolution occurred.

Prof. S. P. Thompson said the gist of Mr. Stanley's paper seemed to be that lights of different colours were concentrated at points situated at different depths in the retina, the violet falling on the part nearest the crystalline lens and the red furthest away. Another view of the action was that the different sensations might be due to the vibrations of longer wave length having to travel greater distances along the nerve terminal before they were completely absorbed.

## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, Monday, February* 6, 1893.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Messrs. Frederick Canton, M.R.C.S., and William Rolle Malcolm.

The Special Thanks of the Members were returned for the following Donations for carrying on investigations on Liquid Oxygen:—Mrs. Bloomfield Moore, £10; Mr. Robert Wilson, £50; Mr. John Bell Sedgwick, £50.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 4, January 23, 1893.

**Contribution to the Study of the Function of Camphoric Acid.**—A. Haller.—The author shows that direct experiments have confirmed the views which he expressed in *Comptes Rendus*, vol. cxiv., p. 1326.

**The Pepto-Saccharifying Power of Blood and of the Organs.**—R. Lépine.—The author considers it probable that the production of sugar in blood in presence of water is preceded by the formation of peptone.

**The Atomic Weight of Palladium.**—A. Joly and E. Leidié.—The mean result of the authors' determinations is 105·438. They purpose re-determining the atomic weights of the metals of the platinum group.

**Action of Alkaline Alcoholates upon Camphoric Anhydride and Certain other Anhydrides.**—P. Cazeneuve.—The ethers of camphoric acid are less easily saponifiable than those of the succinic and phthalic acids. Its anhydride differs from a lactide or a coumarine.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 1.

**Critical Studies on the Methods of Determining Sulphur in Sulphides.**—Leo P. Marchlewski.—This treatise is too bulky for insertion.

**A Rapid Method for the Complete Precipitation of Arsenic as Pentasulphide, and for its Separation from Bismuth, Lead, Antimony, and Analogous Metals.**—Fred Neher.—This paper, according to a footnote, has been translated from an English source. But as it is not stated in what English journal it has appeared it will be inserted in full.

**Determination of Nitrogen in Nitro-Cellulose.**—Edward von Keussler.—This paper requires the accompanying figure.

**Sodium Thiosulphate and Potassium and Potassium Permanganate.**—C. Luckow.—If different quantities of a solution of sodium thiosulphate of known strength are mixed with so much of a solution of permanganate of known strength, that after acidulating the mixture with dilute sulphuric or nitric acid, or after the addition of a solution of potassium or sodium hydroxide, and after boiling the mixture, permanganate or the higher oxides of manganese are still present in solution and in the acid or acidified alkaline solution the excess of permanganate is titrated back with a solution of oxalic acid of equal value, we obtain for equal quantities of sodium thiosulphate equal quantities of the solution of permanganate used for oxidation. From this agreement it appears that the oxidation of sodium thiosulphate by permanganate, whether in an acid or in an alkaline solution, takes place according to fixed rules in the same manner, and that in this case it is suitable for finding a corresponding application for analytical purposes. If the quantities of oxygen required for the oxidation of a known weight of sodium thiosulphate are calculated, it is found that these quantities do not suffice to convert all the sulphur present into sulphuric acid. If, as experiment shows, the solution of permanganate effects a similar oxidation in the solutions of sodium thiosulphate, the quantity of the oxygen required for oxidation is smaller than that needed for converting all the sulphur into sulphuric acid, oxygen compounds of sulphur less rich in oxygen than sulphuric acid are formed at the same time. Sodium thiosulphate, both in acid and alkaline solutions, is therefore converted by permanganate into sodium sulphate and thiosulphate.

**Quantitative Determination of Theobromine in Cacao Beans.** — Dr. P. Jüss.— The "shaking-out" method is that which approximates most closely to the ideal determination of theobromine.

**A Source of Error in the Determination of Phosphoric Acid with Magnesia-Mixture.**—Dr. N. von Lorenz.—The error lies in the omission of citric acid when a little magnesia is simultaneously precipitated.

**The Specific Weight of Aqueous Solutions.**—G. Charpy.—(From the *Comptes Rendus*).

**Relations between the Refraction of Gases and Vapours and their Chemical Composition.**—J. W. Brühl.—Merely mentioned. (From the *Ber. Deut. Chem. Gesell.*).

**Solubility of a Number of Salts in Acetone.**—W. H. Krug and K. P. McElroy.—(From the *Jour. Anal. Chem.*).

**The Behaviour of Some Metals with Gases.**—G. Neumann and F. Steintz (*Monats'hefte fur Chemie*).—This paper will be inserted in full.

**Explanation of the Difficult Solubility of Chemically Pure Zinc in Acids.**—Jul. Weeren (*Ber. Deutsch. Chem. Gesell.*).—Already inserted.

**The most Suitable Form of the Gas-Volumeter.**—G. Lunge (*Zeit. Angew. Chemie*).—For determinations of nitrous and nitric acid, the analysis of saltpetre, guncotton, nitroglycerin, and other esters and salts of nitric acid, the author uses a measuring-tube with a ball, the graduation of which begins at 100 c.c. and extends to 150 c.c. The tube is graduated into tenths of a c.c. All methods founded on the use of the appended flask, such as the analysis of chloride of lime, of manganese ore, permanganate, lead peroxide, the determination of nitrogen in ammonium salts, and in urea with sodium hypobromide, and of nitrogen in the diazo-compounds, can be effected with this apparatus. The determinations of carbonic acid in solids and liquids, with the aid of the author's generating-flask, the determination of carbon in iron and steel, and the standardising of acids for calcium carbonate, can also be effected with this apparatus. By appending Orsat's or Doyère Hempel's absorption-vessels the arrangement is made suitable for the analysis of smoke gases, in which two-thirds of the gas are left as a residue. For other gas analyses a tube holding 100 c.c. is recommended. In most cases the reduction-tube is to be arranged for moist gases by the introduction of a drop of water. For the analysis of nitrose, saltpetre, and dynamite, a dry reduction-tube is used. A measuring-tube holding 50 c.c. graduated from above downwards with a moist reduction-tube, and an especial shaking apparatus, suffices, in the author's opinion, for all the operations required in sulphuric acid works.

## MISCELLANEOUS.

**Bacteriology.**—Mr. W. Heinemann has just issued a "Manual of Bacteriology" by Dr. A. B. Griffiths. It is a work for the laboratory, and contains an account of the latest researches on the subject. The subjects of nitrification, fermentation, ptomaines, germicides, &c., are fully described.

**University College Chemical and Physical Society.**—The Annual Public Meeting will be held at University College, on Friday, Feb. 24, 1893, when an address will be given by Prof. Watson-Smith, F.I.C., F.C.S., entitled "Diseases Incident to Work-People in Chemical and other Industries." The Chair will be taken at 8 o'clock by Prof. F. T. Roberts, M.D. There will be an exhibition of apparatus.

**Recovery of Silver Residues.**—R. Dietel (*Pharm. Zeitung*).—The residues are converted into silver chloride reduced with iron and dilute hydrochloric acid and washed until the chlorine reaction disappears. The silver, containing a little iron, is dissolved in pure nitric acid, the smaller portion is precipitated with boiling soda lye, and the precipitate is washed until a part of the filtrate leaves no residue. The larger portion is evaporated to dryness and then melted until the mass flows quietly. The melt is dissolved in water, filtered from the ferric oxide and slightly concentrated. Any nitrite formed is converted into nitrate by the addition of a small quantity of nitric acid. If the solution is coloured yellow in consequence of the presence of a small quantity of ferric nitrate, the silver oxide mixed with iron oxide, obtained by the treatment of the smaller part of the silver solution, is added, and the whole is boiled until both are transformed into silver nitrate and ferric oxide, *i.e.*, until a filtered and diluted portion gives with potassium ferrocyanide a pure white flocculent precipitate or turbidity. The whole is evaporated to dryness, taken up in water, and again evaporated to dryness.

## MEETINGS FOR THE WEEK.

MONDAY, 13th.—Medical, 8.30.
— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).

TUESDAY, 14th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8. (Anniversary).

WEDNESDAY, 15th.—Society of Arts, 8. "The Detection and Estimation of Small Proportions of Inflammable Gas or Vapour in Air," by Prof. Frank Clowes.
— Meteorological, 7.
— Microscopical, 8.

THURSDAY, 16th.—Royal, 4.30.
— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
— Society of Arts, 3. "The Progress of India Under the Crown," by Sir William Wilson Hunter, K.C.S.I., C.I.E.
— Chemical Society, 8. Ballot for the Election of Fellows. "Platinous Chloride," by W. A. Shenstone. "Melting-points of Compounds of Similar Constitution," by Dr. Kipping. "Electrolysis of Iodic Ethylic Camphorall," by Dr. Walker. "New Base from Corydalis cara," by Dr. Dobbie and A. Lauder.

FRIDAY, 17th.—Royal Institution, 9. "Turacin, a Remarkable Animal Pigment containing Copper," by Prof. A. H. Church, M.A., F.R.S.
— Society of Arts, 8. "The Development and Transmission of Power from Central Stations," by Prof. W. Cawthorne Unwin, F.R.S.
— Geological, 3. (Anniversary).
— Quekett Club, 8. (Anniversary).

SATURDAY, 18th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1734.

# BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE.

By G. KRÜSS and A. LOOSE.

In reference to the feebly basic properties as they occur, especially in scandium, ytterbium, thulium, erbium, holmium, and terbium, the attempt was made to separate this portion of the rare earths from the more strongly basic samaria, didymia, and lanthana under such experimental conditions that the decomposability of the salts of the feebler bases should be increased as far as possible. This is attained if such bases are combined with feeble acids or an opportunity is afforded them of transformation in that direction.

Experiments on the action of potassium nitrite or potassium arsenite proved fruitless. The behaviour of the rare earths with neutral potassium chromate was, however, so remarkable that we wish to describe it. By means of this salt we may, according to the conditions of the experiment, precipitate from a solution of mixed earthy salts either the stronger or especially the feebler bases, and have thus at disposal a peculiarly effective agent for fractionation.

As the following experiments were to explain simultaneously the behaviour of the feeble and the stronger bases with potassium monochromate, an accidental initial material cannot be employed, in which all the earths might, indeed, according to spectroscopic observation, possibly be found, but a part of them might, perhaps, be especially accumulated. A material of yttria earth of medium basicity containing the weaker basic and erbia earths and, on the other hand, the stronger didymia earths in approximately equal quantities, seemed requisite for these experiments.

### *Production of the Initial Material.*

After a part of the didymium and the erbium had been removed from the crude earths derived from the gadolinites of Hitteröe and Ytterby by fractionated precipitation with ammonia, according to G. Krüss (*Liebig's Annalen*, 265, 12), the intermediate fractions were put in hand in a nitric solution. In order to obtain an experimental material of known composition suitable for the intended purpose, the nitrate solutions were next treated with potassium sulphate as follows:—The concentrated solution was mixed with a concentrated solution of potassium sulphate, with the addition of crystals of potassium sulphate, and allowed to stand for two days. After filtration the slight red precipitate was washed with a cold concentrated solution of potassium sulphate, and the earths contained in the precipitate were again converted into nitrates. The filtrate from this first precipitate with potassium sulphate was again submitted to the same treatment with potassium sulphate; this second precipitate yielded a nitrate solution which showed the absorption lines of didymium faintly, but the erbium lines very strongly.

The filtrate from the precipitates of potassium sulphate was resolved into fractions by partial decomposition of the nitrates on heating, the earths of which represented a $\overset{\text{III}}{R}$,* in which the first fraction (containing the feeblest bases) was 105·59, second fraction 104·48, third fraction 100·08, fourth fraction 99·36, fifth fraction 98·2, and sixth fraction (containing the strongest bases) 97·3.

These numbers,* as well as the spectroscopic examination of these fractions, showed that by separating the filtrate from the potassium sulphate precipitates besides some ytterbia and erbia, yttria was chiefly removed, and this earth more uniformly mixed with the stronger as well as with the feebler bases could be obtained from the precipitates with potassium sulphate. Hence the first precipitate with potassium sulphate was submitted to the decomposition of the nitrate by heat.

The first fraction containing the most feebly basic constituents yielded on determining its equivalent a $\overset{\text{III}}{R}=112·96$ and showed the following absorption-spectrum:—

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3.. .. .. | Faint | Di$\alpha$ |
| 654·7.. .. .. | Rather distinct | Er$\alpha$ |
| 640·4.. .. .. | Very faint | X$\alpha$ |
| 579·2.. .. .. | Very faint | Di$\gamma$ |
| 536·3.. .. .. | Very faint | X$\gamma$ |
| 523·1.. .. .. | Very strong | Er$\beta$ |
| 485·5.. .. .. | Distinct | X$\delta$ |
| 452·6.. .. .. | Fading | X$\zeta$ |

The symbols used here and in the following memoirs are the same as those employed for the lines of the rare earths, producing absorption proposed by G. Krüss and L. F. Nilson (*Ber. Deut. Chem. Gesell.*, xx., 2134).

The second precipitation gave a $\overset{\text{III}}{R}=110·74$, and the spectrum:—

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3.. .. .. | Sharp | Di$\alpha$ |
| 654·7.. .. .. | Distinct | Er$\alpha$ |
| 640·4.. .. .. | Distinct | X$\alpha$ |
| 579·2.. .. .. | Fading | Di$\gamma$ |
| 542·6.. .. .. | ,, | X$\beta$ |
| 536·3.. .. .. | ,, | X$\gamma$ |
| 523·1.. .. .. | Broad and strong | Er$\beta$ |
| 485·5.. .. .. | ,, | X$\delta$ |
| 452·6.. .. .. | Very broad and very strong. | X |

| | | |
|---|---|---|
| 3. Fraction | $\overset{\text{III}}{R}=107·4$ | All show the same spectrum, only the line 579·2 Di$\gamma$ gradually increased in strength. |
| 4. ,, | ,, $=105·6$ | |
| 5. ,, | ,, $=104·57$ | |
| 6. ,, | ,, $=104·26$ | |

The residue contained an earth $\overset{\text{III}}{R}=102$, and on spectroscopic examination contained:—

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3.. .. .. | Strong | Di$\alpha$ |
| 679·4.. .. .. | Rather strong | Di$\beta$ |
| 654·7.. .. .. | Faint | Er$\alpha$ |
| 640·4.. .. .. | Faint | X$\alpha$ |
| 626·1.. .. .. | Very faint | Di |
| 579·2.. .. .. | Very strong | Di$\gamma$ |

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* In these experiments we always controlled the composition of the single fractions spectroscopically and simultaneously by determining the equivalents of the earths contained in the fractions. The determining of the combining weights was effected in the manner described in this Journal, iii., 46—55. Shortly before effecting the determination, the earths were again purified in the manner there described.

* For the sake of perspicuity, a table of the basicity of the earths is here appended as resulting from the statements of numerous investigators; it is the foundation of the decomposition of the nitrates. The elements are so arranged that the series begins with the strongest bases and concludes with the feeblest. The atomic weights are appended according to the best determinations:—

| Element. | Atomic Weight. |
|---|---|
| Lanthanum .. .. | 138·88 (Brauner, 1882); 138·01 (Cleve, 1883). |
| Didymium .. .. | 146·58 (Brauner, 1882; also Nilson & Petterson). |
| Samarium .. .. | 150·02 (Cleve); 150·7 (Brauner). |
| Yttrium .. .. .. | 88·9 (Cleve); 1882, 8·902; 1874, 89·5. |
| Terbium.. .. .. | 159·48 (Lecoq de Boisbaudran, 1890). |
| Holmium . .. .. | 160 (Cleve, 1879). |
| Erbium .. .. .. | 166 (Cleve, 1880). |
| Thulium . .. .. | 170·7 (Cleve, 1880). |
| Ytterbium .. .. | 173 (Nilson, 1880). |
| Scandium .. .. | 43·98 (Nilson, 1885; and Robinson, 1884). |
| Cer. as $CeO_2$.. .. | 139·87 (Brauner, 1885; and Robinson, 1884) |

| λ. | Strength of absorption. | Symbol. | |
|---|---|---|---|
| 536·3 | Very faint | $X\gamma$ | |
| 523·1 | Strong | $Er\beta$ | |
| 512·2 | Rather strong | $Di\varepsilon$ | |
| 482 | Distinct | $Di\zeta$ | * |
| 477·7 | Fading | $Sm\beta$ | |
| 469 | Distinct | $Di\eta$ | |
| 463·2 | Rather strong | $Sm\beta$ | |
| 452·6 | Very strong | $X\zeta$ | |
| 445·1 | ,, | $Di\delta$ | |
| 428·5 | Strong | $X\eta$ | |
| 409 | ,, | $Sm\beta$ | |

* Subsequently occur together.

This last portion of the earths worked up after a considerable elimination of yttria, by separating the filtrate of the potassium sulphate precipitates and removal of an excess of erbium and samarium oxide by the first filtering off of the potassium sulphate precipitates still contained sufficient of the latter earths, as well as holmium and didymium earths in approximately equal quantities (judging by the spectrum). At the same time, these earths were still accompanied with considerable quantities of earths of medium basicity of yttria ($\overset{III}{Y}$ = about 90), as may be seen from $\overset{III}{R}=102$.

Exactly the use of such a mixed material, the approximate composition of which is determined by preliminary experiments, will best show the *modus operandi* of the method employed. Hence, this last mentioned material with a $\overset{III}{R}=102$, and the spectrum given in the last table is used as material for the following researches.

(To be continued).

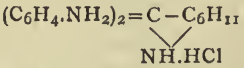
## RESEARCHES ON THE ACID SALTS, AND THE CONSTITUTION OF THE COLOURING MATTERS OF THE ROSALINE GROUP.

By M. A. ROSENSTIEHL.

1. If we are at present quite decided as to the constitution of the bases of the rosaniline group, it is not the same with the bodies which we consider as their salts, and which as colouring matters have acquired an importance of the first rank. I call to mind that according to the classic researches of A. W. Hofmann, rosaniline is the hydrate and magenta the hydrochlorate of a hypothetical triamine, $C_{19}H_{17}N_3$.

E. and O. Fischer, after having discovered the true constitution of rosaniline, and characterising it as triamido triphenylcarbinol, have thought it well to retain Hofmann's hypothesis for the constitution of magenta, and have established the following relation between these two bodies:—

$$\underbrace{(C_6H_4.NH_2)_3=C-OH}_{\text{Rosaniline.}}$$



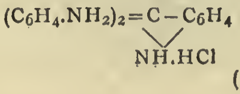
$$(C_6H_4.NH_2)_2=\underset{NH.HCl}{C-C_6H_{11}}$$

That is to say, after having defined the part which belongs to oxygen in the mol. of rosaniline, they do not assign a corresponding function to the chlorine of magenta. According to them it is combined with Hofmann's hypothetical amine in the state of hydrochloric acid.

The object of this paper is not to discuss the reasons for the prevalence of an interpretation, which is neither logical nor simple, but to give the experimental proof that magenta and its congeners, in place of being salts of an amine, are ethers of aromatic amido-alcohols.

2. This manner of regarding the two formulæ—

(1)



$$(C_6H_4.NH_2)_2=\underset{NH.HCl}{C-C_6H_4}$$

and—

(2) $(C_6H_4.NH_2)_3\equiv(C-Cl)$

we see that the former corresponds to a diamine which should be able to unite with 2 mols. of acid, whilst the second contains three times the group $NH_2$, and corresponds to a body which ought to fix 3 mols. of acid.

We know that A. W. Hofmann has prepared and analysed an acid salt of rosaniline which he considers as a trihydrochlorate. This fact would seem to decide the question in favour of formula (1). But if we examine the original memoir (*Proc. Roy. Soc.*, vol. xii., p. 8) we find that Hofmann's affirmation rests upon an interpretation rather than upon precise facts. The analyses, moreover, have not been published. In the saturated salt of a triamine he could not at his epoch see anything but a triacid salt.

3. If we try to prepare the acid trihydrochlorate in a state of purity, according to Hofmann, we easily understand the nature of the difficulty. The hygrometric salt only abandons its water on losing acid. Nevertheless, analysis always shows more chlorine than is required for 3 atoms, but less than 1 mol. to 4 atoms of chlorine.

Only one of these salts, the hydrobromate of hexamethylated rosaniline violet, has been obtained pure by the evaporation of its aqueous solution on the water-bath. A substance of this nature, $C_{20}H_{15}(CH_3)_4N.4HBr_4$, was obtained in 1877 by Brauner and Brandenburg (*Berichte*, vol. x., p. 1845). For the others the moist way had to be abandoned. The colouring matters in the state of chlorides or bromides absorb dry gaseous HCl or HBr, with evolution of heat. Sometimes there occurs fusion,—an accident which must be prevented by mixing the hydracid gas with dry air.

The colouring matters increase in weight, and the quantity of acid absorbed is much greater than necessary to satisfy the chemical affinities. But we obtain compounds of a constant composition by placing the supersaturated matters in a vacuum in the cold over concentrated sulphuric acid. After two or three days the weight no longer varies. The same result is reached more rapidly on exposing the substance in a current of cold dry air.

4. The polyacid salts no longer possess the metallic lustre so characteristic of the colouring matters whence they are derived. Those of rosaniline are not stable; after a few days water no longer dissolves them without residue. The methylic derivatives appear most stable. The aqueous solution possesses the colour of the original colouring matters. But, if instead of dissolving them in water they are allowed to become moist in contact with air, and spread out in a slender layer upon a white saucer, the characteristic colouration of the acid salts appears. The salts of magenta and of malachite green are yellow.

6. The examination of the analytical results leaves no doubt as to the conclusions to be drawn. Triamidic triphenylcarbinol, whether methylated or not, produces acid salts containing 4 atoms of bromine or chlorine; the same tetramethylated diamide carbinol gives rise to salts containing 3 atoms of chlorine or bromine for 2 atoms of nitrogen.

With regard to acids rosaniline and its congeners present two distinct functions: an alcohol function and an amine function. Experiment shows that the alcoholic function predominates, though modified by the propinquity of the group $NH_2$. The basic character is thus increased. The properties of the bases are comparable to those of the metallic protoxides.

The fact is that these amidic ethers undergo double decompositions with the same ease as the mineral salts. They are intermediate between the alkaline bases and the alcohols.

The amine function takes the second rank. We must insist upon this point, that the rosaline is not a triamine,—that function belongs to its ether. In consequence of the presence of the acid radicle in its molecule, the amine character is diminished, and we readily understand the relative instability of these salts.

In fine, if Hofmann has clearly seen the two series of compounds which the acids form with rosaniline, the extreme instability of the saturated salts on the one part and a preconceived idea on the other, did not permit him to recognise that polyhydrochlorate contains 4 atoms of chlorine. The establishment of the fact that 1 mol. containing 3 atoms of nitrogen may enter into reaction with 4 mols. of acid warrants us in concluding that we here encounter a novel function which we may characterise by saying that the colouring-matters of the rosaniline group are ethers of the amidic tertiary aromatic alcohols.—*Comptes Rendus*, vol. cxvi., p. 194.

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### ON THE
## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E., and J. B. HENDERSON.

(Continued from p. 71).

### II.—*Action of Hydrogen on Hot Glass.*

A CURRENT of hydrogen, purified by being passed through a red hot tube full of copper-wire gauze (*vide supra*) was passed through a U-tube containing vitrioled pumice, thence through a combustion tube 300 m.m. long and 15 m.m. wide inside, which was kept at a red heat by means of a combustion furnace, and, from this tube, into a graduated Pisani bottle; and this operation was continued until we felt sure from the volume of gas collected that the hydrogen, as it came out of the combustion tube, must be as free as at all possible, of both water and oxygen (its liability to be contaminated with sulphurous acid was not yet known to us at the time). We then attached to the outlet of the combustion tube two U-tubes charged with vitrioled pumice, of which the first was tared. From the second the gas passed into the Pisani bottle to be measured there. The experiment was continued until 12 litres of hydrogen had passed through the tared U-tube, which was then detached and weighed. In the first four experiments the combustion tube was empty; in the fifth it was filled with fragments of combustion tubing; in the sixth the combustion tube was in the condition in which it had been left by the preceding experiment.

The results were as follows:—

| | Experiment— | | | | | | |
|---|---|---|---|---|---|---|---|
| | I. | II. | III. | IV. | V. | VI. | |
| Time allowed for the 12 litres passing through | 2·5 | 1·5 | 3 | 3·25 | 3·50 | 3·5 | hours. |
| M.grms. of water obtained.. .. | 0·4 | 3·0 | −0·9 | 5·0 | 10·3 | 5·3 | „ |

Experiments I. and III., as we see, yielded practically no water (in No. III., indeed, the U-tube lost 0·9 m.grm.); the 3 m.grm. in Experiment II. may be accounted for by the gas having passed through very rapidly, but the 5 m.grm. produced in Experiment IV. cannot thus be explained away. Suspecting that the water produced in the copper gauze tube had not been completely retained by the U-tube provided for the purpose, we inserted a tared U-tube with vitrioled pumice after it, before proceeding to Experiments V. and VI.; but this additional tube gained only 0·9 m.grm. in V. and 0·8 in VI. The obvious irregularities in the results are probably owing to a small quantity of sulphurous acid produced in the U-tube following the copper gauze; but as this U-tube was only small, we have little doubt that the 10·3 m.grm. of water obtained in V. were at least partly produced by the action of the hydrogen on the hot glass. Admitting this, the fact that only 5·3 m.grm. were obtained in Experiment VI. is easily explained: the available stock of oxygen in the skins of the fragments had been largely exhausted by Experiment V. We will resume these experiments with perfectly oxygen-free hydrogen, such as we subsequently learned to prepare, as soon as we can find the time, because it is important to know whether or not red hot glass is absolutely proof against hydrogen.

### III.—*Syntheses of Water effected with Small Weights of Oxide of Copper.*

Referring to the section headed "Our First Series of Syntheses" (and to Fig. 3) for a description of our apparatus and exact mode of operating, we at once pass to a statement of our results. A glance at the table shows that Experiments I. and II. were absolute blanks, having been made with an empty reduction tube. Under "Oxygen used" we give the loss of weight suffered by the oxide of copper, uncorrected for the displaced air. From it the "water due" is calculated by multiplication with 1·12537 (see under "First Series of Syntheses"). "Surplus hydrogen" means the number of litres of hydrogen which were collected in the "Pisani" bottle while the gas streamed through the hot reduction tube, uncorrected. "Water obtained" means the total weight of water obtained, uncorrected for the displaced air.

| | Experiment— | | | | |
|---|---|---|---|---|---|
| | I. | II. | III. | IV. | V. |
| Oxygen used, m.grms. | 0 | 0 | 291·95 | 324·52 | 415·8 |
| Water due .. .. .. | 0 | 0 | 328·6 | 365·2 | 467·93 |
| Surplus hydrogen used, litres.. .. .. .. | 5 | 3 | 10 | 10 | 9·5 |
| Water obtained, m.grms. .. .. .. | 0·6 | 0·25 | 327·5 | 366·9 | 467·9 |
| Surplus water .. .. | 0·6 | 0·25 | −1·1 | 1·7 | −0·03 |

| | Experiment— | | | | |
|---|---|---|---|---|---|
| | VI. | VII. | VIII. | IX. | X. |
| Oxygen used .. | 426·88 | 4230·25 | 2876·45 | 4805·25 | 621·2 |
| Water due.. .. | 480·41 | 4760·6 | 3237·1 | 5407·6 | 699·08 |
| Surplus hydrogen used .. .. | 9·5(?) | 3 | 3·5 | 3 | 5 |
| Water obtained . | 480·35 | 4761·1 | 3235·9 | 5406·6 | 700·3 |
| Surplus water .. | −0·06 | 0·5 | −1·2 | −1·0 | 1·22 |

#### *Supplementary Experiments.*

XI. In this experiment the "Oxygen used" amounted to 411·9 m.grms., and the reduction was effected with the least sufficient volume of hydrogen. The water obtained weighed 463·6 m.grms.; that is to say, 0·06 more than 411·9 × 1·12537. After the apparatus had been weighed, the parts were again put together, the copper was heated in a litre of hydrogen to make sure of its freedom from oxygen of any kind; only then the water-absorption tubes were appended, and the experiment continued until 10 litres of hydrogen had gone over the heated metal. Of the two vitrioled pumice tubes which followed the reduction tube, the first lost 4·45, the second gained 5·05 m.grms., which anomaly we were not able to explain, and perhaps we had no right to look upon the net gain of 0·6 m.grm. as representing the adventitious water produced from these 10 litres of hydrogen.

XII. Essentially a repetition of No. 11, except that only 3 litres of hydrogen were used in the second stage. "Oxygen used" = 474·35 m.grms.; water due = 533·64; water got = 534·4; excess = 0·57 m.grm. In the second stage the anomaly noticed in No. XI. again presented itself; the first of the vitrioled U-tubes lost 2·6 m.grms., the second gained 3·3; net gain = 0·7 m.grm.

XIII. The copper resulting from XII. was left in the tube over night; it was then re-heated in 3 litres of hydrogen, the water absorption tubes attached, and the experiment continued until 11 litres of hydrogen had gone through the apparatus. The first U-tube lost 2·65 m.grms., the second gained 2·55; net loss = 0·1 m.grm.

XIV. Oxygen used = 609·55 m.grm., water due =

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* *Proceedings of the Philosophical Society of Glasgow.*

685·97; water obtained = 686·30; excess = 0·33 m.grm. In the second stage 12 litres of hydrogen were used, the adventitious water amounted to −1·55+2·8=1·25 m.grm.

XV. and XVI. In these experiments the oxide of copper tube was omitted, and its place taken by a somewhat smaller tube drawn out at both ends, and charged with a scroll of platinum foil. The platinum was heated in the hydrogen for a whole hour before the U-tubes for the absorption of water were attached. The hydrogen from the copper gauze tube passed through two successive U-tubes charged with vitrioled pumice, and the platinum tube was followed by two similar tared U-tubes (1 and 2), and these again by a protection tube to keep out the vapour of water from the Pisani bottle.

| | Experiment— | | |
|---|---|---|---|
| | XV. | XVI. | XVI.A. |
| Hydrogen used.. .. | 10 | 11 | 12 litres. |
| Gain of U-tube 1 .. | 1·5 | 1·0 | 1·7 m.grms. |
| Gain of U-tube 2 .. | 0·2 | −0·15 | 0·1 m.grm. |
| Total water produced | 1·7 | 0·85 | 1·8 m.grms. |

XVII. and XVIII. In these experiments an empty tube was substituted for the one containing the platinum foil; the procedure otherwise was the same as in the case of XV. and XVI.

| | Exp. XVII. | Exp. XVIII. |
|---|---|---|
| Hydrogen used.. .. .. | 10 | 10 litres. |
| Gain of U-tube 1 .. .. | 1·1 | 1·3 m.grms. |
| Gain of U-tube 2 .. .. | −0·2 | −0·5 m.grm. |
| Total adventitious water | 0·9 | 0·8 m.grm. |

At the time when these nineteen experiments were made, we were still in ignorance of the fact that even in the cold hydrogen acts perceptibly on oil of vitriol with formation of sulphurous acid. We were, therefore, quite at a loss to explain the anomaly which presented itself in some of them, that certain U-tubes, which ought to have remained constant or gained weight, lost weight. On the whole, however, we took them as proving that in a synthesis of water carried out with, say 8 grms. or more, of oxygen, the adventitious water produced in the reduction tube amounts to very little provided the hydrogen which enters the reduction tube is really free of oxygen; and ours, we thought, was, because we had passed the gas through a tube full of red hot copper gauze, followed by one or two U tubes charged with vitrioled pumice.

(To be continued).

## MAGNESIUM ZINC-EISEN.

By H. N. WARREN, Research Analyst.

This compound intended solely for pyrotechny is produced either by the electrolysis of magnesium sodium chloride in contact with zinc, or by the action of sodium metal upon that compound. As in the first instance, about ten or twelve pounds of zinc are introduced into a convenient size plumbago crucible, through the bottom of which is inserted a carbon rod; an excess of sodium magnesium chloride is next added, and a current of about 50 volts passed through the whole. The zinc speedily absorbs the magnesium thus set free, while chlorine escapes abundantly from the further electrode in contact with the magnesium chloride.

When an alloy containing about 70 per cent of magnesium has been obtained the current is broken, and a small quantity of ferrous chloride introduced; a further action is thus established, metallic iron being set free, which further alloys with both the zinc and magnesium to the extent of about 12 per cent. By this means a compound is obtained possessing so brittle a texture as to be readily reduced to the finest powder.

In the second instance, a saturated alloy of sodium and zinc is caused to act upon a mixture of magnesium sodium chloride; the sodium speedily changes place with the magnesium, forming the above mentioned alloy, to which an equivalent portion of iron is introduced by the action of ferrous chloride. These alloys are invaluable in photography, for flash-light, and in pyrotechny as signals, being equal to the pure magnesium as a light producing agent, at the same time being produced at a much lower cost.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

## INDUSTRIAL APPLIANCES FOR ELECTROLYSIS OF METALLIC CHLORIDES AND THE OBTAINING OF CHLORINE AND PURE METAL IN A CONTINUOUS MANNER.*

As we know, chlorides can be decomposed by means o a pile current into chlorine and metal. Thus, Bunsen obtained magnesium, then with Mathiessen, barium, strontium, and calcium, by conveying a current of proper intensity into the melted chlorides. H. Ste.-Claire Deville also applied this method with great success to aluminium by treating double chloride of aluminium and sodium.

According to these principles the new apparatus is formed of—

1. A prismatic vat (the shape of which can be altered according to circumstances) of cement on an iron skeleton; the cement can be replaced by substances also refractory to acids.

2. A bell-shaped cap of cement resting on a channel, on the top part of the vat; it dips partially into the electrolyte, so as to assure a perfect hydraulic joining formed by the electrolyte itself.

3. This cap has a pipe for the evolution of chlorine. The electrolytic apparatus being formed by several vats, their evolution pipes all run to a chief conduit, which conveys the chlorine into the apparatus, where it is industrially treated.

Special appliances render a rapid dismounting possible. The cap is raised by means of a crane, and the lead pipe taken from the chief conduit by a movable nut of hardened lead fitted to a special cock.

4. Anodes of agglomerated graphite, artificially made if necessary, by putting cast iron in contact with coal. The current can be taken from the vat either outside or inside.

5. Cathodes formed of thin plates of lead in double sheets, laid crosswise on metallic sheets fixed permanently in the vat; the current is conveyed by these fixed plates.

6. Electrodes arranged at a certain distance from the bottom of the vat in order to avoid interior short circuits in the case where the conductive substances happened to fall to the bottom of the vat, thus re-uniting two neighbouring electrodes.

7. Lead pipes forming fixed cathodes arranged along a rectangular surface constituting a flat serpentine; they take in the vat the place of a certain number of cathodes; they are protected against the action of the chlorine dissolved in the electrolyte by the electrolytic current itself; for they constantly remain in communication with the negative pole.

8. Lead pipes arranged between the different vats uniting them in two's, so as to preserve the condensation degree of the liquid constant by a continuous circulation of the electrolytic solution of the metallic chloride.

9. Tubes on the inside of the receivers intended to expel

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* *Bulletin International de l'Electricité*, Jan. 16, 1893.

the chlorine, by means of a current, as also the air, before the opening of the vat.

10. The parts susceptible of being attacked by chlorine are placed in the centre of the electrolytic bath and protected by the current of the negative pole.

11. A special cock of hardened lead, which enables the dismounting of the vats easily and without loss of chlorine.

12. Vats kept out of reach of the exterior air by wooden cases; the interval between the cases and vats is filled by some substance which is a bad conductor of heat, such as sawdust, wool, &c.

## ANALYSIS OF GADOLINITE.

### (From Llano County, Texas).

By L. G. Eakins.*

| | |
|---|---|
| $SiO_2$ | 23·79 |
| $ThO_2$ | 0·58 |
| $Fe_2O_3$ | 0·96 |
| $Ce_2O_3$ | 2·62 |
| $(DiLa)_2O_3$ | 5·22 |
| $(YEr)_2O_3$ | 41·55 |
| FeO | 12·42 |
| GlO | 11·33 |
| MnO | trace |
| CaO | 0·74 |
| MgO | trace |
| Alkalies | trace |
| $H_2O$ | 1·03 |
| $P_2O_5$ | 0·05 |
| | 100·29 |

In the rare earths from this mineral the absorption spectrum of didymium was strong, and that of erbium was weak. The molecular weight of the oxide $(YEr)_2O_3$ was 260.—*Bulletin of the United States Geological Survey*, No. 64.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, January 19th, 1893.*

Prof. A. Crum Brown, President, in the Chair.

Messrs. James W. Rodger and Morris W. Travers were formally admitted Fellows of the Society.

Ordinary certificates were read for the first time in favour of Messrs. William Thomas Boone, 6, Mount Pleasant Road, Tottenham; Frederick George Fuller, 19, Brunswick Square, W.C.; Arthur John Heath, 1, Grove Villas, Redland, Bristol; Wesley Lambert, 55, Plumstead Common Road, Plumstead; Herbert Bloome Mole, Hillside, Shepton Mallet; Fred. Marsden, Bangor, North Wales; Charles Platt, Buffalo, N.Y., U.S.A.; Charles Henry Southwell, Boston; John Charles Umney, 50, Southwark Street, London; Herbert Wills, LL.D., Fern Bank, Halliwell, near Bolton.

Certificates of the following candidates, proposed by the Council under Bye-law I., para. 3, were also read:—Francis P. Dunnington, Charlottesville, Va., U.S.N.A.; Albin Haller, 14, Rue de Metz, à Nancy; William J. Martin, jun., M.D., Charlottesville, Va., U.S.N.A.; Charles E. Wait, Knoxville, Tenn., U.S.N.A.; Willoughby Walke, Fort Munroe, Va., U.S.N.A.; Henry C. White, Athens, Georgia, U.S.N.A.

### *Address to M. Pasteur.*

On behalf of the Chemical Society of London, we, the President and Officers, beg to tender to you, Mons. Pasteur, our most hearty congratulations on the occasion of your 70th birthday, and to express the fervent hope that for many years to come you may continue to exert your beneficent influence over that department of scientific enquiry so peculiarly your own.

It is thirty years since you were elected a Foreign Member of our Society; and at that time your work as a pioneer was already completed. By your study of the tartaric acids and by the discovery of methods of resolving the optically inactive acid into its active components, you laid the foundation of the modern theories of geometrical isomerism which during recent years have served so largely to promote new and important experimental enquiries; and you placed weapons in the hands of chemists which have retained their usefuleess up to the present day, and which over and over again have been wielded with marvellous effect.

Furthermore, your studies on fermentations—apart from their industrial importance, which is immense—have served to promote enquiries of the utmost value to mankind, and their influence must ever be felt.

Few men have been able to present to the world so imperishable a record of services rendered to humanity; and your name is one which must ever be enshrined in loving memory in the records of time.

We are, Sir, in deepest respect,
Your most faithful colleagues,
A. Crum Brown.
T. E. Thorpe.
Henry E. Armstrong.
John M. Thomson.
R. Meldola.

(*Presented December* 27, 1892).

Of the following papers those marked * were read:—

*93. "*Glucinum.* Part I. *The Preparation of Glucina from Beryl.*" By John Gibson, Ph.D.

Of the many methods proposed for the preparation of glucina from beryl, only a few give satisfactory results, and none of them can be applied easily on a large scale. The percentage of glucinum in beryl is small, and it is therefore necessary to work up large quantities of this very hard mineral in order to obtain a stock of glucina sufficient for the purposes of investigation. Hitherto it has been found necessary to grind the mineral to a very fine powder as a preliminary to its complete decomposition by the usual agents employed in the case of refractory silicates.

The present communication gives an account of a method by which a kilogrm. or more of beryl may be worked up at a time in an easy manner, and without being ground to a fine powder, the whole of the glucina contained in the beryl being obtained very quickly in a nearly pure condition, and, in particular, nearly free from alumina and oxide of iron. The method is based on the different behaviour of the fluorides of aluminium, iron, and glucinum when heated together, it being found that if coarsely ground beryl be heated in an iron vessel with six parts of ammonium hydrogen fluoride, the mineral is completely decomposed at a temperature below a red heat, the soluble aluminium fluoride at first formed being rendered insoluble in water if the heating be sufficiently prolonged, while the bulk of the fluorides of iron are decomposed and converted into ferric oxide, the glucinum fluoride remaining soluble in water.

A new method for the perfect removal of the last traces of iron from the crude glucina is also described, based on the observation that in the presence in solution of a large excess of a lead or mercuric salt the precipitation of the lead or mercury as sulphide by ammonium sulphide effects by mass action the complete precipitation of the iron.

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* Compare Hidden and Mackintosh, *Am. Journ. Sci.*, Dec., 1889.

*94. "*The Determination of the Thermal Expansion of Liquids.*" By T. E. Thorpe, F.R.S.

The author describes improvements in the ordinary dilatometrical method of determining the thermal expansion of liquids. The main improvement consists in the adoption of the simple device now employed in the construction of standard mercurial thermometers, *i.e.*, in enlarging the bore of the tube at some point in the stem, thus forming a small bulb or cavity in order that the position of the 0° and 100° points may be determined on each instrument irrespectively of its range without unduly increasing the length of the stem or diminishing the width of the scale divisions. The length of the stem is thus considerably shortened, so that both it and the thermometer can be wholly immersed in a bath of moderate size; this makes it possible to take successive readings with much greater rapidity than formerly, and obviates the necessity of corrrecting for the emergent columns of the two instruments, thereby diminishing the time and labour required both in the actual observations and the subsequent reductions.

In the paper the mode of constructing and calibrating the dilatometers is fully described, also the mode of cleaning and filling them, the baths used in heating them, and the method of making the observations.

### Discussion.

Professor Ramsay having advocated the method of heating by means of the vapours of liquids boiling under regulated pressures which had been largely used by Prof. Young and himself in place of baths of heated liquid, Professor Thorpe pointed out that the time occupied and labour involved in making the observations was small in comparison with that involved in their reduction, and that, for the purposes of calculation, it was very convenient to take readings at definite intervals of temperature; this, he thought, could be more readily done by means of a liquid bath.

Professor Ramsay said that it was equally easy to vary and adjust the temperature of vapour baths, but admitted that such were not well adapted for use at low temperatures.

*95. "*The Determination of the Thermal Expansion and Specific Volumes of Certain Paraffins and Paraffin Derivatives.*" By T. E. Thorpe, F.R.S., and Lionel M. Jones, B.Sc.

The authors give the data relating to a number of substances, and discuss the results, particularly in relation to Lossen's deductions. Their results are summarised in the Table.

It will be seen that, with the exception of that for propionic anhydride, all the observed numbers differ considerably from those calculated by means of Kopp's values. On the other hand, they show in the main a fairly satisfactory agreement with the values calculated by Lossen's formula. It is noteworthy that the observed value for acetic anhydride deduced from Kopp's experiments, viz., 109·9, is also greatly in excess of the value calculated by Lossen's formula. If, however, Lossen's slightly higher value, *e.g.*, $CO_2H = 10{\cdot}74$, as given for the oxalic ethers, be taken, values for these oxides are obtained which are in better agreement with the results of observation; thus—

| | Observed. | Calculated. |
|---|---|---|
| Acetic anhydride .. .. | 109·9 | 108·4 |
| Propionic anhydride .. | 154·2 | 154·4 |

*96. "*The Hydrocarbons Derived from Dipentene Dihydrochloride.*" By William A. Tilden and Sydney Williamson.

The dihydrochloride $C_{10}H_{16}2HCl$ (m. p. 50°), prepared by the interaction of moist hydrogen chloride and dextro- or levo-rotatory turpentine, is known to be identical with the dihydrochloride formed from dextro- or levo-rotatory citrene (limonene) or from inactive "dipentene." The hydrocarbon obtained by removing the elements of hydrogen chloride from this compound has been supposed to consist essentially of one compound, dipentene, but in view of results obtained in oxidising this substance (*Trans.*, liii., 880), a further examination of the product seemed desirable.

The authors find, by direct experiment, that, like dextrolimonene, when oxidised by nitric acid, levolimonene and pure dipentene afford neither toluic nor terephthalic acid. The product obtained by heating dipentene dihydrochloride with aniline, however, is a mixture of hydrocarbons, of which dipentene is perhaps the most abundant constituent, but is accompanied by large proportions of cymene, terpinene, terpinolene, and a small quantity (about 2·5 per cent) of a saturated paraffinoid hydrocarbon boiling at about 155°. The toluic acid obtained in the former experiments (*loc. cit.*), therefore, is not to be regarded as formed from dipentene, but from the cymene present, and to some extent from the terpinene, which, when oxidised by nitric acid, yields a smaller but appreciable amount of this acid.

The paper concludes with a short discussion of some theoretical points, having reference chiefly to the formulæ which have been ascribed to pinene and camphene.

*97. "*Sulphonic Derivatives of Camphor.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. J. Pope.

The study of these compounds has been entered upon in order, if possible, to throw light on the changes which attend the formation of acetylorthoxylene, &c., from camphor and sulphuric acid (*cf.* Armstrong and Kipping, *Trans.*, 1893, 75).

| | B. p. °C. | Density at 0°. | Density at b. p. | Specific volume. | | |
|---|---|---|---|---|---|---|
| | | | | Obs. | Kopp. | Lossen. |
| Pentane .. .. .. .. | 36·3 | 0·64750 | 0·61200 | 117·6 | 121·0 | 117·2 |
| Isopentane.. .. .. .. | 30·4 | 0·63872 | 0·60857 | 118·3 | 121·0 | 117·2 |
| Isohexane .. .. .. .. | 62·0 | 0·67660 | 0·61744 | 139·3 | 143·0 | 139·8 |
| Amylene .. .. .. .. | 36·4 | 0·68499 | 0·64759 | 108·1 | 110·0 | 109·7 |
| Isoprene .. .. .. .. | 35·8 | 0·6912 | 0·6545 | 103·9 | 99·0 | 102·3 |
| Trimethyl carbinol .. .. | 82·2 | 0·80716 | 0·7194 | 102·8 | 106·8 | 102·0 |
| Dimethyl ethyl carbinol .. | 101·3 | 0·8269 | 0·7248 | 121·4 | 128·8 | 123·4 |
| Inactive amyl alcohol .. | 131·4 | 0·82536 | 0·71362 | 123·3 | 128·8 | 123·4 |
| Active amyl alcohol .. .. | 128·7 | 0·83302 | 0·72111 | 122·0 | 128·8 | 123·4 |
| Methyl ethyl ketone . .. | 80·6 | 0·82961 | 0·74422 | 96·7 | 100·2 | 95·1 |
| Methyl propyl ketone .. | 101·7 | 0·82585 | 0·72568 | 118·5 | 122·2 | 117·2 |
| Diethyl ketone .. .. .. | 102·1 | 0·8335 | 0·7306 | 117·7 | 122·2 | 117·2 |
| Propionic anhydride . .. | 168·6 | 1·0336 | 0·8431 | 154·2 | 53·2 | 150·3 |
| Methyl sulphide . .. .. | 37·5 | 0·87022 | 0·82567 | 75·1 | 77·6 | 75·8 |
| Isobutylene bromide .. | 149·6 | 1·7675 | 1·5147 | 142·6 | 144·2 | 142·8 |

The preparation of camphorsulphonic acid has been attempted by several chemists, but up to the present with a uniform lack of success; the authors found, however, that it may be prepared by the interaction of anhydrosulphuric acid containing about 15 per cent of anhydride and dry powdered camphor: very vigorous action ensues on adding the acid, much heat being liberated, and sulphur dioxide is evolved; on pouring the acid liquid on to ice, very little camphor separates. To purify the product, the sodium salt prepared from the solution is submitted to the action of phosphorus pentachloride, and, by a somewhat tedious process, *camphorsulphonic chloride*, $C_{10}H_{15}O{\cdot}SO_2Cl$, is obtained in colourless crystals which are a mixture of optically different modifications very difficult to resolve. The isolation of a pure sulphonic derivative of camphor in the manner described is by no means easy, several other products being simultaneously formed in large quantities.

According to Marsh and Cousins (*Trans.*, 1891, 967) camphorsulphonic acid is not formed by the interaction of chlorosulphonic acid and camphor dissolved in chloroform. The authors find, however, that camphor is readily sulphonated by chlorosulphonic acid in absence of a solvent; the action proceeds without any noticeable carbonisation or evolution of sulphur dioxide. The sulphonic chloride prepared from this product, like that already referred to, is a mixture of optically different isomerides.

What appears to be the pure dextrorotatory form of the sulphochloride crystallises in tetrahedra melting at 136—137°.

Prior to the isolation of the active chloride, the following derivatives were prepared from a nearly pure inactive product:—

*Camphorsulphonamide*, $C_{10}H_{15}O{\cdot}SO_2NH_2$, obtained by the action of aqueous or alcoholic ammonia on the sulphonic chloride; six-sided, transparent, colourless, monosymmetric plates ($a:b:c = 0{\cdot}821:1:1{\cdot}047$; $\beta = 81° 4'$), melting at 134—135°.

*Camphorsulphonic acid*, $C_{10}H_{15}O{\cdot}SO_3H$. The sulphonic chloride is slowly hydrolysed by boiling water; the acid crystallises in arborescent forms, and is very deliquescent; it melts at 58—60°. Its aqueous solution dissolves zinc or magnesium with evolution of hydrogen; a series of well-defined salts has been obtained.

The action of anhydrosulphuric acid on the haloid derivatives of camphor is much less violent than when camphor itself is employed. Anhydrosulphuric acid dissolves bromocamphor with slight rise of temperature, giving an amber-coloured solution of sulphonic acid completely soluble in water. The sodium salt, prepared in the usual way, gives on treatment with phosphorus pentachloride a *bromocamphorsulphonic chloride*,—

$$C_{10}H_{14}BrO{\cdot}SO_2Cl,$$

which can be separated from a quantity of dark oil accompanying it by suitable methods. The purified substance crystallises from chloroform in magnificent octahedra, melting at 136—137°. The crystals are colourless and transparent, and may be readily obtained several centimetres in diameter.

Marsh and Cousins (*Trans.*, 1891, 974) have prepared a sulphonic chloride of similar composition by the action of chlorosulphonic acid on bromocamphor. They describe the substance as "a black semi-crystalline solid." A repetition of their work showed this substance to be merely an impure form of the one now described; the identity of the chlorides from the two sources having been established by the ordinary means and by crystallographic measurements. The chloride has a high rotatory power—$[\alpha]_D$ = about $+128°$ in chloroform solution.

*Bromocamphorsulphonic acid*, $C_{10}H_{14}BrO{\cdot}SO_3H$, is readily obtained by boiling the chloride with water. It forms large pyramidal shaped crystals, which are somewhat hygroscopic and very soluble in water. The anhydrous acid melts at 195—196°; the aqueous solution dissolves zinc and magnesium. The acid is described by Marsh and Cousins as a "black tarry mass." The salts generally crystallise well, and have been examined crystallographically. The *sulphonamide* crystallises in long silky needles, and melts at 144—145°.

*Chlorocamphorsulphonic chloride*, $C_{10}H_{14}ClO{\cdot}SO_2Cl$, obtained in an analogous manner, crystallises in massive colourless octahedra, indistinguishable in appearance from the bromo-derivative. It melts at 123—124°. $[\alpha]_D$ = about $+110°$ in chloroform solution. This substance was described by Marsh and Cousins (*loc. cit.*) as a "microcrystalline black solid."

On boiling with water the chloride yields *chlorocamphorsulphonic acid*, $C_{10}H_{14}ClO{\cdot}SO_3H$, which crystallises in hygroscopic rectangular plates; it affords a series of well-defined salts.

The *ammonium* salts of bromo- and chloro-camphorsulphonic acids are especially interesting from a crystallographic point of view. Possessed of optical activity when in solution, they crystallise in monosymmetric prisms exhibiting hemimorphism and showing strongly marked pyroelectrical properties.

The further investigation of these sulphonic derivatives, and of the by-products which are formed in their preparation, is in progress.

98. "*The Preparation of Dinitro-α-naphthylamine* $[NH_2:NO_2:NO_2 = 1:2:4]$, *from its Acetyl and Valeryl Derivatives.*" By R. Meldola, F.R.S., and M. O. Forster, Ph.D.

A simple method of preparing this compound was described by one of the authors in a note published in 1886 (*Ber.*, xix., 2683); other investigators having experienced difficulties, or having altogether failed, in obtaining it by this method, we have been led to reinvestigate the subject, and can confirm the practicability of the process formerly described. The difficulty experienced by other workers has, no doubt, arisen from using the hydrolysing agent (sulphuric acid) either too strong or too weak. The following details may, therefore, be found useful:—

The α-acetnaphthalide is nitrated in glacial acetic acid in the usual way, using a little more than the theoretical quantity of fuming nitric acid. It will be found advantageous to divide the operation into two stages, adding one-half of the nitric acid to the well-cooled solution in the first place, and then allowing to stand over night, so that the mixed mononitro-α-acetnaphthalides are formed at a low temperature. The solution is warmed the following day in a water-bath till the crystalline mononitro-derivatives have dissolved up, when the other half of the nitric acid is added. The dinitro-derivative soon forms, and the solution begins to solidify while still hot. The whole mass forms a pulp of crystals when cold. The mother-liquor being squeezed out, the crystals are washed with water, drained, and purified by being boiled up with alcohol and allowed to cool. Very little of the dinitro-α-acetnaphthalide is lost by this treatment, as the compound is but slightly soluble in cold alcohol. Resinous impurities, which interfere with the purity of the subsesequent product, are removed by the alcohol. The alcoholic extraction may be repeated if necessary. The purified dinitro-derivative, when dry, is easily hydrolysed by heating to the temperature of boiling water for about an hour with a mixture of equal volumes of strong sulphuric acid and water (50 grms. dinitro-compound, 150 c.c. strong sulphuric acid, and 150 c.c. of water). The product is poured into cold water, collected, washed, and crystallised from somewhat dilute alcohol with the addition of animal charcoal till it has the correct melting-point (237° from alcohol).

While engaged in these experiments, it appeared to be of interest to ascertain the effect of lighter and heavier acid radicles in facilitating or retarding hydrolysis by sulphuric acid. It was found that *formonaphthalide* could not be converted into a dinitro-derivative in glacial acetic acid. Even when a large excess of nitric acid is used, the product is mononitroformonaphthalide. Nitrogen found: (I.) 13·08, (II.) 12·99 per cent; calculated for mononitro-derivative, 12·96 per cent; calculated for dinitro-derivative, 16·09 per cent.

It evidently consists of a mixture of isomerides, as no compound of a definite melting-point was isolated; much resin is also formed during the nitration.

*Valeronaphthalide* was prepared by boiling α-naphthylamine with excess of "anhydrous valerianic acid" (Hopkin and Williams) for at least thirty-six hours. The product fuses to an oil under hot water, and is purified by successive agitation with hot water, dilute ammonia, dilute chlorhydric acid (to remove unaltered naphthylamine), and finally with water. The resinous cake thus obtained gradually becomes a crystalline mass on standing in the cold. One or two crystallisations from dilute alcohol render the compound sufficiently pure for nitration. A specimen was purified for analysis by repeated alternate crystallisations from alcohol and benzene. The pure compound forms white silky needles melting at 125 to 126°, and gradually becoming violet on exposure to air and light: on analysis, it was found to contain 78·95 carbon, 7·72 hydrogen, and 6·25 nitrogen, the values calculated for $C_{10}H_7 \cdot NH \cdot C_5H_9O$ being 79·29 carbon, 7·48 hydrogen, 6·17 nitrogen.

The nitration is easily effected by dissolving the substance in glacial acetic acid and at once adding to the cold solution a little more than the theoretical quantity of fuming nitric acid diluted with an equal volume of glacial acetic acid. It is best to start with a cold *saturated* solution of the valeronaphthalide in glacial acid. After adding the nitric acid, the solution may be allowed to stand for some hours in the cold and then warmed to 70—80° for about fifteen minutes. The nitration is complete by that time, the dinitro-derivative slowly separating out on cooling. The crystalline cake thus obtained is first washed with water and then purified by crystallisation from alcohol, in which the dinitro-derivative is much more soluble than the corresponding dinitro-acetnaphthalide. If, during nitration, decomposition sets in with effervescence, the contents of the vessel must be at once cooled, or the product will be found to be much contaminated with resinous matter, and the yield will be considerably diminished. Two experimental batches were lost by neglecting this precaution.

*Dinitrovaleronaphthalide*, when purified by crystallisation from alcohol and glacial acetic acid successively, forms pale straw coloured silky needles, having a melting point of 218°. It is rapidly converted into dinitro-α-naphthol by boiling with dilute alkali. A purified specimen was analysed with the following results:—Carbon 57·03, hydrogen 4·96, nitrogen 13·11. The values calculated for $C_{10}H_5(NO_2)_2 \cdot NH \cdot C_5H_9O$ being:—Carbon 56·78, hydrogen 4·73, nitrogen 13·24

This compound appears to be more readily hydrolysed than the acetyl derivative. The proportions of acid, water, and substance found effective were:—30 grms. dinitro compound, 600 grms. strong sulphuric acid, 60 grms. water; after heating from 10—15 minutes in a water-bath, the product is precipitated by pouring the mixture into cold water and treating as in the case of the acetyl derivative. We have not made a series of exact comparisons between the acetyl and valeryl derivatives with the object of measuring the relative rates of hydrolysis. It appears, however, from our experiments, that valeryl is more easily removed than acetyl without deeper decomposition of the dinitro-derivative into resinous products, and this seems to point to the conclusion that there is an advantage in starting with a naphthalide containing a radicle *heavier* than acetyl. On the other hand, glacial acetic acid is so much cheaper than its higher homologues, that from an economical point of view the dinitro-α-acetnaphthalide will be found the most advantageous compound to employ for the preparation of dinitro-α-naphthylamine. It is proposed to prepare a large quantity of the latter by the method described, with the object of extending our knowledge of the meta-di-derivatives of naphthalene, for the preparation of which the metadinitronaphthalene, obtained by the diazo-method, will, it is hoped, furnish a convenient source. We have received valuable assistance in conducting these experiments from Messrs. E. M. Hawkins and F. B. Burls, two of the third year students of the Finsbury Technical College, to whom we wish to express our thanks.

99. "*Thionyl Bromide.*" By P. J. Hartog and W. E. Sims.

The authors have prepared thionyl bromide by the interaction of sodium bromide and thionyl chloride, obtaining it in the form of a deep crimson liquid of the relative density 2·68 at 18° C.; the colour is, however, possibly due to the presence of a small quantity of certain sulphur bromides: though their amount is small, hitherto it has not been found possible to deprive thionyl bromide of these impurities. At 150° thionyl bromide undergoes a complex decomposition, yielding bromine and sulphur bromides. It is extremely hygroscopic and must be preserved in sealed tubes.

100. "*Desulphurisation of the Substituted Thioureas.*" By Augustus E. Dixon, M.D.

Some years ago (*C. S. Trans.*, 1889, 618) the author pointed out that certain disubstituted paraffinoid thioureas are not desulphurised when boiled with an alkaline solution of a lead salt: having since obtained data concerning a considerable number of thioureas, the following conclusions are drawn as to their behaviour with the agent in question:—

1. The monosubstituted thioureas are all desulphurised.
2. The tri- (and probably also the tetra-) substituted thioureas are not.
3. Disubstituted thioureas containing one or more benzenoid groups are desulphurised, but not if such groups be absent.

In the case of thioureas containing the allyl group, the results are less sharp than where alkyl residues are concerned; in the case of the former a trifling separation of lead sulphide is occasionally observed, but the amount produced varies from *nil* to enough to slightly darken the mixture; the effect in these cases is attributed to the difficulty encountered in obtaining the allyl derivatives in a pure condition.

The following compounds are described:—

sym.-*Diisobutylthiourea*, $CSN_2H_2(C_4H_9)_2$.—Colourless rhombic plates, melting at 87—88°.

*Di-(sec.)-butylthiourea*, $CSN_2H_2(C_4H_9)_2$.—Small colourless prisms, melting at 100—101° (uncorr.).

*Methyl-(sec.)-butylthiourea*, $CSN_2H_2(CH_3)(C_4H_9)$.—Flattened rhombic crystals, melting at 79—80°.

*Ethyl-(sec.)-butylthiourea*, $CSN_2H_2(C_2H_5)(C_4H_9)$.—Brilliant flattened crystals, melting at 57—58°.

*Phenyl-(sec.)-butylthiourea*, $CSN_2H_2(C_6H_6)(C_4H_9)$.—Long colourless needles; m. p. 100—101° (uncorr.).

*Diisoamylthiourea*, $CSN_2H_2(C_5H_{11})_2$.—Brilliant small white prisms; m. p. 72—73°.

*Methylisoamylthiourea*, $CSN_2H_2(CH_3)(C_5H_{11})$.—Beautiful vitreous rhombs; m. p. 75—76°.

*Ethylisoamylthiourea*, $CSN_2H_2(C_2H_5)(C_5H_{11})$.—White crystalline mass, melting at 45—46°.

*Phenylisoamylthiourea*, $CSN_2H_2(C_6H_5)(C_5H_{11})$.—Vitreous rhombic glates, melting at 101—102° (uncorr.).

(To be continued).

Kopp Memorial Lecture.—An Extra Meeting of the Chemical Society willl be held on Monday, Feb. 20, at 8 p.m., the Anniversary of the death of Hermann Kopp, when a lecture will be delivered by Prof. Thorpe, F.R.S. The chair will be taken by Lord Playfair.

## NOTICES OF BOOKS.

*A Manual of Bacteriology.* By A. B. Griffiths, Ph.D., F.R.S., F.C.S. London: Heinemann, 1893.

This volume forms one of a series entitled "Heinemann's Scientific Handbooks," of which five volumes have already appeared. The author, Dr. Griffiths, is favourably known to the majority of our readers from the chemical and chemico-physiological papers which have appeared in the Chemical News, the *Comptes Rendus*, and elsewhere, as well as from his independent works.

By a remarkable and not altogether fortunate coincidence this volume has appeared almost simultaneously with Dr. P. F. Frankland's treatise, covering substantially similar ground and enforcing the same views.

In his opening chapter, the author gives Koch's four canons for deciding whether a micro-organism is the cause of any given disease. He then goes on to a survey of physiological experimentation, or as it is vulgarly called, vivisection, in which he concedes rather too much to that class of people whom the late Professor Sir Richard Owen aptly termed "bestiarians."

With the author's general nomenclature we find ourselves unable to agree. He restricts the name microbes to minute vegetable organisms, and even takes it as a synonym for bacteria. Now, if we look at the etymology we shall see that microbes or microbia are micro-organisms either of animal or vegetable character. He thinks that it must be to some extent consolatory to know that the disease germs which invade our bodies are not animals. We should find in this fact very little comfort. The only satisfactory circumstance is that plants have not yet been invested by our hysterical agitators with "equal rights." Were the germ of tetanus, *e.g.*, an animal, to destroy it with disinfectants would, perhaps, be denounced as an outrage. Their wonderful potentialities are explained in a very interesting manner.

In the second chapter, we have an account of the Edinburgh Bacteriological Laboratory and its fittings. This establishment works well considering its unfavourable environment. More fortunate is the Pasteur Institute in Paris, founded and endowed at the cost of £100,000.

In treating of the microscope, Dr. Griffiths recommends the monocular instrument. He suggests that a sheet of black paper should be placed near the eye not in use. We have found it very convenient to take a large old-fashioned spectacle frame, cover one of the glasses, for the eye which is not to be used, with a piece of black paper, and remove the other glass altogether.

Next we find the methods of cultivating microbia, the processes for staining, methods of mounting specimens, and the origin, classification, and identification of species.

Of course, on the origin of microbia little can be said. We have heard it surmised that they may have been conveyed from other worlds through the depths of space. This theory has the advantage that it cannot easily be either proved or disproved. It is, however, possible that if bacteria once landed on this terrestrial ball they may have repeated the invasion. We suggest this notion to epidemiologists as a hypothesis to account for new and mysterious diseases.

This work will be a valuable addition to the library of the hygienist.

*Electrical Experiments.* A Manual of Instructive Amusement. By G. E. Bonney, author of "The Electro-Plater's Handbook," "Induction Coils," &c. With 144 Illustrations. London and New York: Whittaker and Co.

This work, dealing in a clear practical and, though popular, thoroughly sound manner with magnetism and electricity, will doubtless meet with numerous and attentive readers.

The author teaches by the experimental method. He does not invite students to seek for definitions of magnetism and electricity, but lets them ascertain what these agencies can do and what they cannot do, and in this manner guides them to find out their nature better than by a "game at definitions."

*The Principles of Theoretical Chemistry:* with Special Reference to the Constitution of Chemical Compounds. By Ira Remsen, Professor of Chemistry in the Johns Hopkins University. Fourth Edition, thoroughly Revised. London: Baillière, Tindall, and Cox. Philadelphia: Lea Bros. and Co., 1893.

This excellent and well-known treatise gives room for very little comment. It has been fully brought up to the present level of the science, and is enriched with an additional chapter on solution. Perhaps the only exception which may be legitimately taken to the work is that in expounding the periodic law the merit of Newlands is underrated, and that of Mendeleeff, and still more that of Lothar Meyer, exaggerated.

## CORRESPONDENCE.

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—The letter which has been addressed to me by Professor Thorpe, and which was sent by him for publication in your columns last week, has of necessity not yet come before a meeting of the Council of the Institute; but as the statement of his views has been given to the chemical world, I am compelled to request that, without delay, you will suffer me to correct what I consider to be an inaccurate rendering of what actually occurred at the last Council Meeting of the Institute, and of the inferences to be deduced therefrom.

The resolution, of which notice had been given, was moved by Dr. Teed as follows:—

> "That in future the letters F.C.S. be omitted in the Register from all names of members of the Institute."

It was moved as an amendment by Mr. M. Carteighe, seconded by Mr. F. J. M. Page, and carried—

> "That in future all letters indicating membership of any society except the Royal Society (London) be omitted in the Register from all names of Members of the Institute."

It was moved as an amendment by Professor T. E. Thorpe, seconded by Mr. R. J. Friswell, and lost—

> "That all letters denoting membership of societies and degrees be deleted from the list of Members of the Institute."

It was moved as an amendment by Mr. A. H. Allen, seconded by Prof. T. E. Thorpe, and lost—

> "That the words 'except the Royal Society (London)' be omitted."

The original amendment was then put as a substantive motion and carried.

From this it will be seen that the amendment which was carried finally as a substantive motion was brought forward by two gentlemen whom I am certain Professor Thorpe would be willing to recognise among those who have shown themselves zealous supporters of the present mode of election into the Chemical Society, and zealous friends of the Chemical Society. I will go further and say for myself that while in the Chair I have never exercised my right to vote except on the rare occasions when a casting vote has been required, but had I been on the other side of the table on the occasion referred to, I should have voted for this amendment which covers the original motion. I state these facts in order to show that at least some of those whom he will, I trust, continue to recognise as his friends do not share his opinion in this matter, and that the action taken by the Council of the Institute is not the action of any section of its members.

The Council of the Institute *does* "know that it has no power to compel any of the Members of the Chemical Society to omit the letters F.C.S. after their names," but it has power over its register, and can regulate at will how many or how few letters it will admit there, and Professor Thorpe is on this point wrongly informed.

Professor Thorpe asserts that the Council of the Institute has put itself in an attitude of antagonism to the Chemical Society. This I emphatically deny. By thus calling public attention to the fact that he has decided to retire from the Institute, and in stating his reasons for retirement, Professor Thorpe forgets some important points in its history. At the Inaugural Meeting of the Chemical Society held in 1841, the objects of the Society were defined to be:—"The promotion of Chemistry and of those branches of Science immediately connected with it, by the reading, discussion, and subsequent publication of original communications, also the formation of a Chemical Library and Museum," and in the Charter the Chemical Society was declared to have been established "for the general advancement of Chemical Science."

Throughout the Charter and the bye-laws there is not one word relating to the election of Fellows which shows that any standard has at any time been set up by the Society by which the professional attainments of candidates for election could be estimated, and it is a matter of common knowledge that candidates of the most various qualifications are and have always been admitted into the Society. This being the case, a public meeting was held in 1876 at Burlington House, at which a committee was appointed to confer with the Council of the Society upon the question of establishing an organisation among chemists, which should stand toward the profession of chemistry in the same relation as that occupied by the Colleges of Surgeons and Physicians toward medicine. The result of the Conferences with the Council of the Chemical Society was that it was found impracticable for various reasons to establish a section of the Society for the purposes contemplated. Hence it became necessary to establish an independent association in the foundation of which some of the most distinguished Fellows of the Chemical Society were closely concerned.

The Association existed for some years under the Company's Acts and in 1885 received the Royal Charter. In the Charter of the Institute its object is defined to be not "the advancement of Chemical Science" by any direct operation, but in view of the importance of forming a body of "persons properly trained, and that their qualifications should be attested by certificates of competency," and seeing that "at present there is no institution or corporate body which has power to issue such certificates," the Institute was established.

As everybody knows, the persons who now constitute the Institute of Chemistry are on the one hand those who were originally incorporated as having rights to recognition, and on the other hand, younger men who are required to pass through a course of study extending over not less than three years and to pass certain examinations. The business of the Chemical Society, then, is to promote the study of chemical science; the function of the Institute is to carry out that which the Chemical Society could not do, namely, to register persons possessing certain well defined qualifications. When, therefore, Professor Thorpe states that "there is no greater inherent value or property in the letters F.I.C. than in those F.C.S." he is talking nonsense.

I am ready still to maintain, as I have done publicly, that the doors of the Chemical Society should remain open to the amateur, whoever he may be, who will engage to subscribe faithfully to the declaration which every Fellow signs upon the occasion of his admission. But I think it may be questioned whether the use of the letters F.C.S. upon professional cards and in advertisements by *soi disant* analytical chemists is not a breach of their obligation. And when these letters come to be put forward by applicants for public appointments as evidence of professional qualification, it is time that the Council of the Chemical Society, to say nothing of the Institute, should take steps to prevent an imposition upon the public ignorance.

Can it be maintained that the use of letters under the present conditions of admission into the Chemical Society is necessary for the welfare of the Society, and the advancement of the high purposes it has in view? I think not. Else how is it that the other chemical societies of the world get on very well without them and the Physical Society of London, which is properly the sister society, prospers without any such addition?

It is a serious blow to the Institute that a man in the high position of Professor Thorpe should withdraw from its ranks, but his ardour in the cause of the great Society in which he holds the honourable office of treasurer has, I venture to think, led him to extend something less than justice to the efforts which are being made towards the satisfactory organisation of the profession. The influence which the leading scientific chemists might fairly be expected to exercise upon the proceedings of the Institute can only be exercised effectively while they remain members of that body. To withdraw is merely to leave the field to the enemy.

I must not conclude without explaining that this letter is addressed to you in my private capacity. Living, as I do, at a distance from London, I am placed at the disadvantage of being unable to confer, as I should have wished to do on such an occasion, with my colleagues, and I am desirous, therefore, of stating to them and to you that I do not profess now to be acting as the mouthpiece of the body of which I am temporarily President.—I am, &c.,

William A. Tilden.

Birmingham, Feb. 14, 1893.

## THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—With reference to the letter of Professor Thorpe published in the Chemical News, vol. lxvii., p. 71, will you allow us, as the mover and seconder of the amended resolution referred to in that letter, to deny absolutely that it "is practically directed against the Fellows of the Chemical Society," as stated by Professor Thorpe.

No such feeling of disloyalty to the Chemical Society existed or exists in our minds, and it was because the majority of the Council held the same view that our *amended* resolution was passed instead of the original resolution.—We are, &c.,

M. Carteighe.
Frederick Jas. M. Page.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 5, January 30, 1893.

On Certain Articles of Copper of very Ancient Date derived from the Explorations of M. de Sarzec in Chaldea.—M. Berthelot.—Some of the articles found throw further light on the existence of a "copper age," prior to the bronze age. M. Berthelot has examined in particular a votive figure supposed belonging to an epoch prior to the Fortieth Century, B.C. The metal contained neither silver, bismuth, antimony, zinc, nor magnesium, but merely traces of lead, arsenic, and sulphur, along with a little lime and carbonates. It may be considered as copper, industrially pure. At its epoch bronze and tin were not yet worked either in Chaldea or Egypt.

**The Pathogenic Properties of Soluble Substances Elaborated by the Microbe of the Contagious Peripneumonia of the Bovidæ, and on their Value in the Diagnosis of the Chronic Forms of this Malady.**—S. Arloing.—Cultures of the microbe from injection proved fatal to oxen within five to six hours, in the proportion of 0·064 grm. per kilo. of the living weight.

**The H and K Rays in the Spectrum of the Solar Faculæ.**—G. E. Hale.—This paper will be inserted in full.

**Decomposition of the Alkaline Aluminates in Presence of Alumina.**—A. Ditte.—On contact with crystals of hydrated alumina, potassium aluminate is gradually decomposed and its alumina is separated as $Al_2O_3,3H_2O$ (Gibbsite). The same phenomenon occurs with sodium aluminate. This explains the industrial process for preparing alumina from sodium aluminate by agitating a solution of this compound with the crystallised aluminium hydrate.

**Electrometric Study of Acid Potassium Triplatohexanitrite.**—M. Vèzes.—This paper requires the insertion of the two accompanying graphic representations.

**Action of Watery Vapour upon Ferric Chloride.**—G. Rousseau.—There is a complete analogy between the decomposition of ferric chloride in vapour by gaseous water and that of its concentrated solutions. The products obtained in both cases at corresponding temperatures have the same compositions, have the same optical characters, and are similarly destroyed by the prolonged action of boiling water.

**Two Combinations of Cuprous Cyanide with Alkaline Cyanides.**—E. Fleurent.—The author obtains a blue compound, dicuprous-diammonium ammonium cyanide, $2Cu_2Cy_2.CyNH_4.2NH_3.3H_2O$, and a green compound, cupro-dicupric diammonium cyanide—

$$2CuCy_2.Cu_2Cy_2.2NH_3.3H_3O.$$

**The Composition of Some Hydrated Alkaline Phenates.**—M. de Forcrand.—The author's results differ from those of Roméi.

**Researches on the Acid Salts, and on the Constitution of the Colouring-Matters of the Rosaniline Group.**—A. Rosenstiehl.—(See p. 76).

**Analysis of Officinal Creosotes, Gayacol.**—A. Béhal and E. Choay.—One of the two products in question, the creosote of wood-tar, is a complex mixture of phenols and phenolic ethers. The other, gayacol, is a definite chemical compound. The indications given for the analysis of the former kind are merely physical and colour reactions. The authors base their procedure on the following principles:—1. Hydrobromic acid completely demethylates at ordinary pressures the methylic ethers of the phenols. 2. The monophenols are easily carried away by a current of steam. 3. A current of steam does not appreciably remove the polyphenols. 4. Ether entirely removes pyrocatechine and homopyrocatechine from an aqueous solution, and also removes the monophenols. 5. Benzene separates almost quantitatively pyrocatechine from homopyrocatechine. Pure gayacol is a white crystalline solid, melting at 28·5° and boiling at 205·1°.

**Apparatus for Estimating Precipitates by an Optical Method.**—E. Aglot.—This paper will be inserted in full.

**The Pre-Existence of Gluten in Wheat.**—M. Balland.—The author refutes the hypothesis of Weyl and Bischoff that gluten is formed by the simultaneous action of water and ferments.

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**Modified Forms of Berthelot's Calorimetric Bomb.**—Scheurer-Kestner, Meunier-Dollfus, and Pierre-Mahler (*Bull. de Mulhouse* and *Comptes Rendus*).—This paper requires the five accompanying figures.

**A Refractometer.**—E. H. Amagat and F. Jean (*Beiblätter zu den Annalen der Physik und Chemie*).—The apparatus depends on the same principle as the liquoscope of Soudén, *i.e.*, the deviation of a mark observed through a prism filled with the liquid in question.

**An Improved Thermo-Column.**—M. Gülcher (*Berg. und Hutten Zeit.*).—The instrument is durable; cheap, and not exposed to injury from a sudden increase of gaseous pressure.

**Working with the Filter-Press.**—H. Wilde (*Chem. Zeit.*).—The author combines with the filter-press a cylindrical pressure vessel which can bear a pressure of several atmospheres.

**A Shaking-Machine.**—W. R. Dunstan and T. S. Dymond.—(From the Chemical News).

**A New Air-Bath.**—Maunsel White and F. R. Bennet.—(From the *Jour. Anal. Chem.*).

**Fusion Cones.**—Cramer (*Thon-Industrie*).—These cones are devised to indicate the temperatures reached in brick burning.

**The Presence of Hypochlorous Acid in Chlorine Water obtained from Chloride of Lime and Hypochlorous Acid.**—K. Kock.—Hypochlorous acid is present only if the reaction is too violent. For the detection of the hypochlorous acid the chlorine water is shaken up with an excess of metallic mercury. If hypochlorous acid is present there is formed along with mercurous chloride a soluble oxychloride which is detected in the filtrate by means of sulphuretted hydrogen.

**Recovery of Silver Residues.**—R. Dietel (*Pharm. Zeitung*).—Already inserted.

**Simultaneous Precipitation of Copper and Antimony by the Galvanic Current.**—W. Hampe (*Chem. Zeit.*).—This paper will be inserted in full.

**Detection and Determination of Arsenic.**—Joh. Thiele (*Liebig's Annalen*).—This memoir will be inserted in full.

**Detection of Small Quantities of Tartaric Acid and Citric Acid.**—L. Crismer (*Bull. Soc. Chim.*).—The author shows the different behaviour of the two acids with ammonium molybdate in presence of hydrogen peroxide. Citric acid gives no colour, but tartaric acid, even in very small quantities, produces a blue colouration. If we mix 1 grm. pulverised citric acid with 1 c.c. 20 per cent solution of molybdic acid, add from 2 to 3 drops of pure dilute hydrogen peroxide (¼ to 1·5th per cent $H_2O_2$), and heat for three minutes on the water-bath with repeated agitation, we obtain in the absence of tartaric acid a pure yellow colour, whilst in presence of 2 m.grms. tartaric acid there appears a very distinct blue colour which is perceptible even with 1 m.grm.

**Determination of Carbon in Organic Substances in the Moist Way.**—K. Okada (*Archiv. f. Hygiene*).—This paper will be inserted as early as possible.

**A Source of Error in the Ultimate Analysis of Organic Substances.**—G. Neumann.—Ignited copper turnings are capable of absorbing or combining with hydrogen and carbon dioxide. The view of Thudichum, Hake, and Vortmann, that carbon dioxide is capable of expelling hydrogen, was not confirmed. If copper spirals are reduced in methyl- or ethyl-alcohol, an absorption also takes place.

**A Modification of the Dumas Process for the Determination of Nitrogen.**—F. Blau (*Monats'hefte fur Chemie*).—This memoir requires the two accompanying figures.

**Oxygen in Unroasted Ores.**—W. Hampe (*Chemiker Zeit.*).—The author has analysed many lead and copper ores from the Upper Harz, and found in them oxygen which would not have been expected in such unroasted stones. For determining the oxygen 5 grms. of the stone finely powdered and dried at 100° were placed in a weighed bulb-tube of sparingly fusible glass, and then cautiously heated in a current of dry carbon dioxide in order to remove every trace of moisture. After weighing, pure dry oxygen is passed through the tube, and the bulb is heated for a long time to redness, when water escapes. When the reduction is completed, the tube cooled, and the hydrogen expelled by air, it was weighed again. As on reduction in a current of hydrogen, a little sulphur is always carried away as hydrogen sulphide, the tube, during the experiment, is always connected with a vessel containing an alkaline solution of lead. The lead sulphide formed is filtered off and converted into lead sulphate. From the weight of the latter the sulphur is calculated. The loss of weight of the tube, *minus* the weight of the sulphur escaped as sulphuretted hydrogen, gave the weight of the oxygen.

**Reaction of Nitrogenous Organic Substances.**—H. Aufschläger (*Monats'hefte fur Chemie*).—This communication chiefly concerns the amides of carbonic acid, uric acid, and their derivatives, the albumenoids, &c. If such compounds are mixed with zinc-powder and heated in a combustion-tube, there is formed among other products zinc cyanide, $Zn(CN)_2$, permanent in heat, the cyanogen in which can be recognised in the usual manner. This reaction is not analogous to the formation of cyanogen on heating nitrogenous organic compounds with potassium, since, unlike the latter, it is not common to all organic compounds. For a qualitative recognition the solid compounds are mixed with zinc-powder and heated in the tube to incipient redness. Liquids are passed in the form of vapour over the metallic compound at incipient redness. When cold the zinc-powder is extracted with soda-lye and tested in the usual manner for cyanogen with ferric chloride and ferrous sulphate and subsequent addition of hydrochloric acid. Quantitative experiments showed that in the mean 50 per cent of the nitrogen present are obtained in the state of cyanogen.

## MEETINGS FOR THE WEEK.

Monday, 20th.—Medical, 8.30.
—— Chemical, 8. (Extra Meeting). "Kopp Memorial Lecture," by Prof. T. E. Thorpe, F.R.S.
—— Society of Arts, 8. "The Practical Measurement of Alternating Electrical Currents," by Prof. J. A. Fleming, F.R.S. (Cantor Lectures).
Tuesday, 21st.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
—— Pathological, 8.30.
—— Society of Arts, 3. "Wall-Papers and Stencilling," by T. R. Spence.
Wednesday, 22nd.—Society of Arts, 8. "Old Age Pensions," by T. Mackay.
—— British Astronomical Association, 5.
—— Geological, 8.
Thursday, 23rd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
—— Institute of Electrical Engineers, 8.
Friday, 24th.—Royal Institution, 9. "Electrical Railways," by Dr. Edward Hopkinson, M.A.
—— Physical, 5. "A Handy Folometer," by Prof. J. D. Everett, F.R.S. "Plane and Spherical Sound Waves," by Dr. C. V. Burton. "Motion of a Perforated Solid in a Fluid," by G. H. Bryan, M.A.
Saturday, 25th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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### NOTE ON THE
## SUPERSATURATION OF SOLUTIONS OF OXYGEN IN WATER.

By C. A. SEYLER, B.Sc.

The determination of free oxygen in water is of interest and importance; but as much time must frequently elapse between the drawing of the sample and the analysis, there is often a considerable rise in temperature before it reaches the analyst. One is therefore troubled by the doubt as to whether the rise of temperature has caused a loss in the oxygen dissolved. Having frequently noticed that the dissolved oxygen is much higher than corresponds to saturation at the temperature of the water on arrival, I made some experiments to test the point. A recent paper by A. H. Gill (*Jour. Anal. App. Chem.*, vi., No. 11) induces me to contribute my experience on this important matter, which fully agrees with his results.

The experiments show that in a sample of water, as usually delivered in Winchester quarts nearly full, a rise of some 10° C. is without noticeable effect on the dissolved oxygen. The gaseous solution remains supersaturated, and only parts with the extra oxygen upon vigorous shaking in half empty Winchesters. The experiments were made by the convenient method of Thresh (*Jour. Chem. Soc.*, March, 1890), on the water of the Swansea Supply, which is soft and organically pure.

*Series I.*

|  | Temp. °C. | Oxygen, c.c. per litre. | (Roscoe and Lunt). Saturated at |
|---|---|---|---|
| On arrival | 5 | 9·49 | 1°, 9·48 c.c. |
| Raised without shaking to | 9·5 | 9·49 | 1°, 9·48 ,, |
| After shaking at | 13 | 7·26 | 13°, 7·28 ,, |

*Series II.*

|  |  |  |  |
|---|---|---|---|
| On arrival | 9 | — | — |
| On analysis | 13 | (*a*) 8·23<br>(*b*) 8·11 | 7·5°, 8·22 ,,<br>8°, 8·13 ,, |
| After shaking at | 13 | 7·27 | 13°, 7·28 ,, |
| Again raised to | 19 | 7·17 | — |
| After shaking at | 20 | 6·28 | 20°, 6·28 ,, |

*Series III.*

|  |  |  |  |
|---|---|---|---|
| Shaken at | 13 | (*a*) 7·38<br>(*b*) 7·42 | 13°, 7·28 ,,<br>— |
| Raised to | 26·5 | 7·42 | — |
| Shaken at | 26·5 | 5·62 | 26·5°, 5·64 ,, |

In each case a stoppered bottle was nearly filled with the water, and the temperature raised 5° or 6° in the first two series, and 13·5° in the last, without loss of oxygen occurring. As a check on the analysis, the water was reduced to saturation by shaking and blowing air through it; in the last two cases both before and after raising the temperature, and determining the oxygen.

The results show the importance of knowing the temperature of the water at the time of taking the sample, but unfortunately, like other important local particulars, it is not always easy to obtain.

Technical Institute, Swansea.

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**The Atomic Weight of Cadmium.**—W. L. Lorimer and E. F. Smith.—The authors have electrolysed potassium cadmium cyanide. The mean result is 112·055. —*Zeit. fur Analytische Chemie.*

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## BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE.

By G. KRÜSS and A. LOOSE.

(Continued from p. 76).

An acid solution of the earthy nitrates was treated with potassa-lye until there appeared a very slight permanent precipitate. The liquid was filtered off so as to ensure the possession of a neutral solution. It gave with $K_2CrO_4$ a yellow, flocculent precipitate resembling aluminium hydroxide. If it was heated, the precipitation was considerably increased, and the yellow colour of the liquid turned to an intense red, the colour of $K_2Cr_2O_7$. To work up this precipitate it was filtered, the deposit washed and dissolved in hydrochloric acid; the addition of alcohol and the application of heat effected the reduction of the chromic acid. In the green solution the acid was partially neutralised with ammonia, so that the earths could be precipitated by oxalic acid.

The filtrate from the first chromate precipitate was treated twice more in the same manner to ascertain whether potassium chromate acted dissimilarly on different earths; whether this method was altogether suitable for fractionated precipitation. The thought suggested itself that the feeblest bases could be least saturated with so feeble an acid as the chromic, and would therefore be most readily precipitated.

The oxalates obtained from the first chromate precipitation were ignited, but to our surprise the colour of the ignited oxides was brown, and showed a large proportion of didymium. This seemed very striking, since didymia as the strongest base should be the last to fall down. The determination of the equivalent, which for the earths of the initial material showed $\overset{\text{III}}{R}=102$, gave for this first chromate precipitate $\overset{\text{III}}{R}=115·6$. In the second and third precipitate the colour of the earths became paler again; we found $\overset{\text{III}}{R}=111$ and $\overset{\text{III}}{R}=104·3$. Whether the amount of the $\overset{\text{III}}{R}$ obtained as such represented the average earths of the three fractions or was exclusively due to the quantity of didymia present, we may learn by a consideration of the spectra:—

*First Fraction.*

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3 | Very strong | Diα |
| 679·4 | Distinct | Diβ |
| 654·7 | Trace | Erα |
| 640·4 | ,, | Xα |
| 579·2 | Extremely strong | Diγ |
| 523·1 | Very strong | Erβ |
| 512·2 | Distinct | Diε |
| 482 | ,, | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |
| 463·2 | ,, | Smβ |
| 445·1 | Very strong | Diδ |
| 452·6 | Faint | Xζ |
| 536·3 | Very faint | Xγ |
| 428·5 | Rather distinct | Xη |
| 409 | Rather strong | Smβ |

*Second Fraction.*

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3 | Very distinct | Diα |
| 679·4 | Very faint | Diβ |
| 840·4 | Trace | Xα |
| 579·2 | Very strong | Diγ |
| 523·1 | Very distinct | Erβ |
| 512·2 | Faint | Diε |
| 482 | ,, | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 463 | Faint | Smβ |
| 452·6 | Distinct | Xζ |
| 445·1 | Faint | Diδ |

### *Third Fraction.*

| | | |
|---|---|---|
| 728·3 | Distinct | Diα |
| 579·2 | Faint | Diγ |
| 523·1 | Distinct | Erβ |
| 512·2 | Faint | Diε |
| 445·1 | Very faint | Diδ |

As it is easy to see in the first fraction, the didymium and erbium oxides, *i.e.*, exactly the strongest and the weakest of the bases occurring in the material, are simultaneously accumulated. Yttrium, with its reducing effect on the atomic weight, appears only in the following fractions. This remarkable fact leads to the following considerations.

The red colour of the solution observed on heating is evidently due to the formation of acid potassium chromate. This may take place either, as it was supposed, by a part of the salts losing chromic acid and being converted into a basic salt or hydroxide; two cases are here probable:—

1. Only the feeble bases are decomposed; the decomposition then ensues in the inverse proportion of the basicity.
2. All the bases are simultaneously decomposed.

Against the latter assumption it must be considered that yttrium appears only in the latter of the above named fractions.

In favour of the second case it must be considered that in the first fraction didymium and erbium were precipitated together. But the possibility must not be overlooked that Di might be precipitated as a sparingly soluble salt, whilst the more feebly basic Er was thrown down as a basic compound.

On this point we could only reach certainty by sometimes increasing the decomposition of earthy salts and sometimes reduced to a minimum by the application of different temperatures. The portions precipitated in the cold were therefore examined separately from those deposited on heating.

A fresh portion of the same material ($\overset{\text{III}}{R}=102$) was mixed with potassium chromate, with careful refrigeration, as long as a perceptible increase of the precipitate was observed. The precipitate was filtered off, the yellow filtrate heated, and the solution thus strongly reddened was separated from the precipitate formed. The filtrate of this second precipitate thrown down in heat was then treated twice in the same manner, forming thus three fractions, each of which is divisible into a portion precipitated in the cold, and one thrown down in heat.

From the equivalents of the earths as found, we calculated the following values for $\overset{\text{III}}{R}$ in the single fractions, the absorption spectra of which are appended.

### *First Fraction.*

*A.—Precipitated in the Cold*, $\overset{\text{III}}{R}=120{\cdot}9$.

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3 | Very strong | Diα |
| 679·4 | Distinct | Diβ |
| 579·2 | Extremely strong | Diγ |
| 523·1 | Very strong | Erβ |
| 512·2 | Fading | Diε |
| 482 | Distinct | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |
| 463·2 | ,, | Smβ |
| 445·1 | Extremely strong | Diδ |
| 428·5 | Very strong | Xη |
| 409 | Broad, fading | Smβ |

*B.—Precipitated in Heat*, $\overset{\text{III}}{R}=111{\cdot}7$.

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3 | Strong | Diα |
| 679·4 | Faint | Diβ |
| 579·2 | Strong | Diγ |
| 523·1 | ,, | Erβ |
| 512·2 | Faint | Diε |
| 445·1 | Rather strong | Diδ |
| 452·6 | Very distinct | Xζ |

### *Second Fraction.*

*A.—Precipitated in the Cold*, $\overset{\text{III}}{R}=113$.

| | | |
|---|---|---|
| 728·3 | Strong | Diα |
| 679·4 | ,, | Diβ |
| 579·2 | ,, | Diγ |
| 523·1 | ,, | Erβ |
| 512·2 | Faint | Diε |
| 482 | Strong | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |
| 463·2 | ,, | Smβ |
| 445·1 | Very strong | Diδ |

*B.—Precipitated in Heat*, $\overset{\text{III}}{R}=107$.

| | | |
|---|---|---|
| 728·3 | Strong | Diα |
| 679·4 | Distinct | Diβ |
| 654·7 | ,, | Erα |
| 640·4 | ,, | Xα |
| 579·2 | Strong | Diγ |
| 536·3 | Thin and sharp | Xγ |
| 531·3 | Very faint | Di |
| 523·1 | Very strong | Erβ |
| 512·2 | Fading | Diε |
| 482 | Distinct | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |
| 463·2 | ,, | Smβ |
| 452·6 | Very distinct | Xζ |
| 445·1 | Very strong | Diδ |
| 428·5 | Distinct | Xη |

### *Third Fraction.*

*A.—Precipitated in the Cold*, $\overset{\text{III}}{R}=107{\cdot}6$.

| | | |
|---|---|---|
| 728·3 | Very strong | Diα |
| 708 | Very faint | Di |
| 679·4 | Faint | Diβ |
| 579·2 | Very strong | Diγ |
| 523·1 | Strong | Erβ |
| 512·2 | Fading | Diε |
| 482 | Rather strong | Diζ |
| 477·7 | ,, | Smβ |
| 469 | ,, | Diη |
| 463·2 | ,, | Smβ |
| 445·1 | Very strong | Diδ |
| 428·5 | Trace | Xη |

*B.—Precipitated in Heat*, $\overset{\text{III}}{R}=102{\cdot}4$.

| | | |
|---|---|---|
| 728·3 | Strong | Diα |
| 679·4 | Faint | Diβ |
| 654·7 | Distinct | Erα |
| 579·2 | Strong | Diγ |
| 523·1 | Very strong and sharp | Erβ |
| 512·2 | Fading | Diε |
| 482 | Very faint | Diζ |
| 477·7 | ,, | Smβ |
| 469 | Distinct | Diη |
| 463·2 | Very faint | Smβ |
| 445·1 | Rather strong | Diδ |

Residue: $\overset{\text{III}}{R}=99{\cdot}8$.

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3.. .. .. | Rather strong | Diα |
| 679·4.. .. .. | Very faint | Diβ |
| 654·7.. .. .. | ,, | Erα |
| 579·2.. .. .. | Rather strong | Diγ |
| 523·1.. .. .. | ,, | Erβ |
| 512·2.. .. .. | Faint | Diε |
| 482 .. .. .. | Very faint | Diζ |
| 477·7.. .. .. | ,, | Smβ |
| 469 . .. .. | ,, | Diη |
| 463·2.. .. .. | ,, | Smβ |
| 445·1.. .. .. | Rather strong | Diδ |

It will be seen from these tables that didymium it chiefly concentrated in the cold precipitations, whilst the hot precipitations contain relatively more erbium.* As the same time, the determinations of the equivalents of the elements precipitable in heat give always smaller combining weights than the cold precipitations,—a sign that yttria $(\overset{\text{III}}{Y}=89-90)$ was thrown down to a small extent in the cold precipitations but in larger quantities in the precipitations given by potassium chromate in heat. Yttria, according to spectroscopic observations, is chiefly accompanied by the more feebly basic erbia. The new separation on heating solutions precipitated with $K_2CrO_4$ is, in fact, a consequence of the feeble basicity of these earths, and considered in conjunction with the red colouration of the solutions,—a sign of the decomposition.

Potassium chromate, therefore, acts upon the nitrate solution of the rare earths in a twofold manner: in cold chiefly as a precipitant for didymium chromate, but in heat as an agent for the separation of the basic erbium and didymium compounds. These distinctions are far remote from being utilised for the quantitative separation of these earths. We possess, indeed, hitherto no even approximately accurate method for the quantitative separation of the oxides of this group. Still, neutral potassium chromate is perhaps peculiarly applicable in working up rare earths, since by alternating precipitation in cold and heat we may separate alternately from a mixture of these oxides the stronger and then again the weaker bases, and thus attack the earths to be separated from two different sides.

(To be continued).

## MANURIAL EXPERIMENTS WITH TURNIPS.†

By C. M. AIKMAN, M.A., B.Sc., F.R.S.E.,
Lecturer on Agricultural Chemistry, Glasgow and West of Scotland Technical College, and Glasgow University Extension Board.

(Concluded from p. 68).

The last series of experiments were those carried out by Mr. James Fulton on his farm at Balshagray, Whiteinch, near Glasgow.

The experimental plots were situated in the centre of a large field with a fair southern exposure, and on perfectly level ground. The soil is described by Mr. Fulton as "a good loam with a touch of clay in it."

The past history of the field since 1885 is as follows:—

1885. Turnips, which received 40 tons farmyard manure to the acre.
1886. Wheat, which received no manure.
1887. Hay, which received nitrate of soda.
1888. Potatoes, which received 15 tons farmyard manure and 3 cwt. special artificial potato manure.

The plots were eleven in number, and consisted each of 1-20th of an acre in extent; each plot being three yards wide—containing four drills—and running from north to south.

The manures used in these experiments consisted of slag, superphosphate, and farmyard manure. Owing to a mistake, nitrate of soda was forgotten to be applied. The variety of turnip used in this case was the Purple Top Swede. The manures and the turnips were sown on the 22nd of May. There was no rain for five days after sowing. They were thinned on the 21st of June, and lifted on the 19th of November.

The following Table exhibits the quantities of manures and returns of turnips yielded by the different plots:—

| No. | Manure. | Produce. | | Increase over nothing plots. | |
|---|---|---|---|---|---|
| | | Tons. | cwt. | Tons. | cwt. |
| 1. | Nothing .. .. .. .. | 16 | — | — | — |
| 2. | 6 cwt. slag .. .. .. | 17 | 5 | 1 | 5 |
| 3. | 2½ cwt. super .. .. .. | 16 | 10 | — | 10 |
| 4. | 12 cwt. slag .. .. .. | 18 | — | 2 | — |
| 5. | 5 cwt. super .. .. .. | 17 | 15 | 1 | 15 |
| 6. | 4 cwt. slag and 10 tons dung .. .. .. .. | 20 | 10 | 4 | 10 |
| 7. | 4 cwt. slag and 10 tons dung .. .. .. .. | 20 | 10 | 4 | 10 |
| 8. | 6 cwt. slag and 10 tons dung .. .. .. .. | 20 | — | 4 | — |
| 9. | 6 cwt. slag and 10 tons dung .. .. .. .. | 20 | 10 | 4 | 10 |

The largest increase will be seen in plot No. 9, receiving 6 cwt. slag; but between this plot and plots Nos. 6 and 7—receiving 4 cwt. of slag and 10 tons dung—there is practically very little difference.

The largest increase is in plots Nos. 5 to 9, receiving different quantities of slag along with 10 tons of dung, the plots receiving the smaller quantity of slag showing an equal increase to those receiving the larger quantity of slag. With regard to the plots receiving slag and super alone, it will be seen that in both cases the slag gives distinctly better results than the super. The following Table exhibits the cost of the manures and the value of the increase. The turnips were sold at 16s. per ton:—

| No. | Manure. | Cost. | Value of increase in crop. |
|---|---|---|---|
| 2. | 6 cwt. slag .. .. .. | £0 6 0 | £0 19 6 |
| 3. | 2½ cwt. super .. .. | 0 6 10 | 0 8 0 |
| 4. | 12 cwt. slag .. .. .. | 0 12 0 | 1 12 0 |
| 5. | 5 cwt. super.. .. .. | 0 13 8 | 1 8 0 |
| 6. | 4 cwt. slag and 10 tons dung . .. .. .. | 3 4 0 | 3 12 0 |
| 7. | 4 cwt. slag and 10 tons dung .. .. .. | 3 4 0 | 3 12 0 |
| 8. | 6 cwt. slag and 10 tons dung .. .. .. | 3 6 0 | 3 4 0 |
| 9. | 6 cwt. slag and 10 tons dung . .. .. .. | 3 6 0 | 3 12 0 |

These figures show again that the most profitable manure is the slag; and that the farmyard manure, even applied at the rate of 10 tons an acre, did not pay.

*N.B.*—The following Table contains the results of all the experiments in a convenient form.

The following conclusions may be drawn from the results of these experiments:—

1. That while farmyard manure is valuable in giving the crop a good start and bringing it well forward during the period of germination and early growth by supplying a certain amount of easily assimilable plant food, and, in the case of dry weather, attracting a quantity of moisture, it is not profitable—as far as first year's results are concerned—when applied in such quantities as 20 or even 10 tons per acre.

2. That the basic slag proved by far the most economical of the manures used; and that, further, the

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* The X lines, excepting Xη, likewise appear chiefly in the hot precipitations, as may be seen from the second fraction (*B*).

† From the *Transactions of the Highland and Agricultural Society of Scotland.*

| Manures. | | | Cost. | Increase in crops over nothing plots. | Value of increase. | Profit. | Value of increase due to dung. | Cost of dung. | Value of increase due to nitrate. | Cost of nitrate. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tons. | cwt. | £ s. d. | Tns. cwt. qr. | £ s. d. | £ s. d. | £ s. d. | £ s. d. | £ s. d. | £ s. d. |
| Slag .. | 0 | 6 | 0 6 0 | 2 8 0 | 1 9 0 | 1 3 0 | — | — | — | — |
| ,, .. | 0 | 6 | 0 6 0 | 8 19 0 | 4 13 0 | 4 7 0 | — | — | — | — |
| ,, .. | 0 | 6 | 0 6 0 | 1 5 0 | 0 19 6 | 0 13 6 | — | — | — | — |
| ,, .. | 0 | 12 | 0 12 0 | 9 14 0 | 3 17 6 | 3 5 6 | — | — | — | — |
| ,, .. | 0 | 12 | 0 12 0 | 7 0 0 | 4 4 0 | 3 12 0 | — | — | — | — |
| ,, .. | 0 | 12 | 0 12 0 | 2 0 0 | 1 12 0 | 1 0 0 | — | — | — | — |
| Super .. | 0 | 2½ | 0 6 10 | 0 10 0 | 0 8 0 | 0 1 2 | — | — | — | — |
| ,, .. | 0 | 4 | 0 11 0 | 4 5 0 | 2 11 0 | 2 0 0 | — | — | — | — |
| ,, .. | 0 | 4 | 0 11 0 | 10 17 3 | 4 6 0 | 3 15 0 | — | — | — | — |
| ,, .. | 0 | 8 | 0 13 8 | 1 15 0 | 1 8 0 | 0 14 4 | — | — | — | — |
| ,, .. | 0 | 8 | 1 2 0 | 6 8 0 | 3 17 0 | 2 15 0 | — | — | — | — |
| ,, .. | 0 | 8 | 1 2 0 | 11 12 0 | 4 13 0 | 3 11 0 | — | — | — | — |
| ,, .. | 0 | 9 | 1 5 0 | 3 18 0 | 2 15 0 | 1 10 0 | — | — | — | — |
| Slag ..<br>Dung .. | 0<br>15 | 6<br>0 | 4 16 0 | 16 10 1 | 6 12 0 | 1 16 0 | 1 19 0 | 4 10 0 | — | — |
| Slag ..<br>Dung .. | 0<br>10 | 6<br>0 | 3 6 0 | 4 0 0 | 3 4 0 | (loss)<br>0 2 0 | 2 4 6 | 3 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>10 | 6<br>0 | 3 6 0 | 4 10 0 | 3 12 0 | (gain)<br>0 6 0 | 2 12 6 | 3 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>10 | 4<br>0 | 3 4 0 | 4 10 0 | 3 12 0 | 0 8 0 | 2 19 0 | 3 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>10 | 4<br>0 | 3 4 0 | 4 10 0 | 3 12 0 | 0 8 0 | 2 19 0 | 3 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>20 | 6<br>0 | 6 6 0 | 9 3 0 | 5 10 0 | (loss)<br>0 16 0 | 4 1 0 | 6 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>20 | 12<br>0 | 6 12 0 | 11 15 0 | 7 1 0 | (gain)<br>0 9 0 | 5 12 0 | 6 0 0 | — | — |
| Slag ..<br>Dung .. | 0<br>15 | 12<br>0 | 5 2 0 | 17 16 2 | 7 2 8 | 2 0 8 | 3 5 2 | 4 10 0 | — | — |
| Slag ..<br>Dung .. | 0<br>20 | 14<br>0 | 6 14 0 | 7 18 0 | 5 11 0 | (loss)<br>1 3 0 | 0 11 0 | 6 0 0 | — | — |
| Super ..<br>Dung .. | 0<br>20 | 5<br>0 | 6 13 9 | 16 8 0 | 9 17 0 | (gain)<br>3 3 3 | 8 9 0 | 6 0 0 | — | — |
| Super ..<br>Dung .. | 0<br>20 | 7<br>0 | 6 19 0 | 7 13 0 | 5 6 0 | (loss)<br>1 13 0 | 3 3 3 | 6 0 0 | 4 6 0 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>20<br>0 | 7<br>0<br>1 | 6 17 0 | 10 3 0 | 7 2 0 | (gain)<br>0 5 0 | — | — | 2 19 0 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>20<br>0 | 14<br>0<br>1 | 7 4 0 | 11 3 0 | 7 16 0 | 0 12 0 | — | — | 2 8 6 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>15<br>0 | 6<br>0<br>1 | 5 6 0 | 19 17 3 | 7 19 0 | 2 13 0 | — | — | 0 17 4 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>15<br>0 | 12<br>0<br>1 | 5 12 0 | 20 0 1 | 8 0 0 | 2 8 0 | — | — | 2 11 0 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>20<br>0 | 6<br>0<br>1 | 6 16 0 | 13 18 0 | 8 1 0 | 1 5 0 | — | — | 1 3 0 | 0 10 0 |
| Slag ..<br>Dung ..<br>Nitrate.. | 0<br>20<br>0 | 12<br>0<br>1 | 7 2 0 | 14 8 0 | 8 13 0 | 1 11 0 | — | — | 2 11 6 | 0 10 0 |

larger quantities of slag proved more profitable than the smaller.

3. That superphosphate of lime was also a profitable manure, and that, as in the case of the slag, the larger quantities gave better results than the smaller.

4. That nitrate of soda in every case showed itself to be a most profitable manure.

**The Determination of Sulphur in Combustibles by the Eschka Process.**—This method has been discussed in the "Bulletin of the Engineers' Society of Western Pennsylvania." According to Mr. Jas. Handy the Eschka process furnishes identical results both in its original form and in the modification introduced by Dr. Hundeshagen, which latter presents no advantages. Another chemist present, Mr. Jas. Camp, confirmed the results of Mr. Handy.—*Rev. Univ. des Mines*, xx, No. 2.

ON THE

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E., and J. B. HENDERSON.

(Continued from p. 78).

### *Effect of Vitrioled Pumice on Hydrogen Gas.*

To form an idea of the extent to which Dumas's syntheses may have been vitiated by the formation of sulphurous acid in the vitrioled pumice tubes which he used for drying his hydrogen, we produced a continuous current of Dumas's hydrogen and determined the volume of a standard solution of permanganate which a given volume of the gas decolorised.

As a necessary preliminary, a current of hydrogen,

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* *Proceedings of the Philosophical Society of Glasgow.*

which had been purified only by passing it through the acetate of lead, the nitrate of silver, and the caustic potash tubes of the Dumas's set, was sent through a quantity of acidulated water which had been just barely reddened by addition of a drop of permanganate. After the gas had been going through for four hours, the reagent had turned brownish through partial reduction of the $Mn_2O_7$ to $MnO_2$; hence it was proved that pure hydrogen does not act sufficiently on permanganate to prohibit the projected method of analysis.

This point being settled, the two long vitriol tubes were appended to the Dumas's set, the hydrogen turned on, and kept going until all the air was sure to be expelled. The following set of successive apparatus (see Fig. 7) was then appended to the outlet of the last vitriol tube:—A test-tube, B, containing some water and dilute sulphuric acid; a similar test-tube, C, charged with alkaline permanganate; two small successive U-tubes, D and E, charged, the first with fragments of caustic potash, the second with vitrioled pumice; and lastly, a test-tube, F, similar to B and C. The test-tubes B and F both communicated with a burette containing standard permanganate. From the outlet of F the gas passed into a graduated Pisani bottle to be measured there. The apparatus being adjusted, hydrogen was passed through it, and the sulphurous acid contained in the gas titrated as it came by occasional addition of permanganate from out of the burette so as to maintain a distinct red colouration in the respective liquids. The maintenance of the end reaction, however, became more and more difficult as the experiment progressed, on account of the formation of precipitates of $MnO_2$ in the reagents.

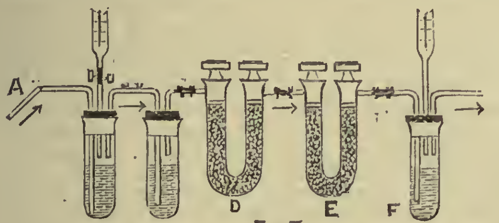

Fig. 7.

In all, 12 litres of gas were passed through the apparatus, and, as far as we were able to determine the $SO_2$, it amounted to 4·8 m.grms. in test-tube B, and to 0·48 m.grm. in F. These numbers of course could be looked upon only as rough approximations.

Hence, in a *Second Experiment*, the sulphurous acid in the gas was determined more exactly by passing it through 8 c.c. and 4 c.c. of permanganate (1 c.c. = 5·572 m.grm. of iron) contained in two successive Erlenmeyer flasks, B and C (substituted for the test-tubes previously used), besides some sulphuric acid, and determining the $SO_2$ absorbed at the end of the experiment by adding a known excessive weight of standardised ferrous sulphate and titrating back with the permanganate. The tube F received 0·3 c.c. of permanganate, which were just decolorised by the 10 litres of gas which passed through the apparatus in three hours. The $SO_2$ absorbed in B and C amounted to 11·89 m.grms., or to 1·19 m.grm. per litre. Before this experiment was started the Dumas's set of purifying tubes, including the two terminal vitriol tubes, had been standing filled with hydrogen for two days.

Hence, in a *Third Experiment*, those two tubes were emptied out, and the vitrioled-pumice fragments evaporated to dryness in a platinum basin; fresh vitriol was then poured on them, and the greater part of this again was chased away by evaporation. The pieces of pumice were then lifted out by means of a platinum forceps, replaced in their tubes, and the experiment then started without unnecessary delay. The residual vitriol in the basin was tested for sulphurous acid and found pure. In 3·5 hours 18 litres of hydrogen were passed through. The $SO_2$ formed amounted to 16·4 m.grms., or to 0·91 m.grm. per litre of gas.

Dumas's syntheses, as we are told, often took over twelve hours for their completion; hence, in all those cases in which vitriol was used as a dehydrating agent, the hydrogen must have been contaminated with sulphurous acid. For every 2 m.grms. of $SO_2$ which passed over Dumas's red-hot oxide of copper, the residual copper contained 1 m.grm. of sulphur as $Cu_2S$, and the water collected included 1·125 m.grm. of water produced from the oxygen of the sulphurous acid. Supposing the loss of weight suffered by the reduction tube amounted to S, and the weight of $SO_2$ acting upon the oxide of copper was $= n$, the oxygen which produced the W parts of water obtained amounted to $S + \frac{n}{2} + \frac{n}{2} = S + n$ parts. Hence we have for the true value $k_0$ of the ratio $H_2O : O$,

$$k_0 = \frac{W}{S+n} = \left(\frac{W}{S} = k\right) \times \frac{1}{1+n/S}.$$

For a guess at the correcting factor, let us take $S =$ 8000 m.grms., and assume that the hydrogen used for the conversion of that oxygem into water amounted to 12 litres; whence $n = 12 \times 0{\cdot}91$ by Experiment III. Hence $1 : (1 + \frac{n}{S}) = 1 - 0{\cdot}001365$. Now, according to our calculation, Dumas's value for $k$, uncorrected for adventitious oxygen, was $= 1{\cdot}12547$; hence we have by the formula, $k_0 = 1{\cdot}12393$, and for $H_2 : O$ the number $0{\cdot}12393$.

Those of Dumas's syntheses, in which phosphoric anhydride was used instead of oil of vitriol, ought to be free of the sulphurous acid error, but we do not find any confirmation of this in his tabular statement of results; hence we presume that the phosphoric anhydride was used only as an auxiliary to oil of vitriol.

Some time after these experiments had been made, it struck us that we had better make sure of our theory of the effect of the sulphurous acid in the hydrogen on the results of a synthesis of water. After some pioneering work, the following method was adopted and carried out:—

A combustion-tube, charged with pure reduced copper, was made to communicate, by its outlet end (indirectly *vide infra*), with a graduated Pisani bottle, and by its inlet end with a two-way glass stopcock communicating with a Kipp (charged with zinc and dilute sulphuric acid) in such a manner that we were able to let the hydrogen go by either of two prescribed ways (see Fig. 10). The hydrogen was purified by passing it, first through a large tower filled with pieces of caustic soda, and then through a tube full of red-hot copper gauze. If the gas went one way, it entered the combustion tube containing the reduced copper as it was; if it went the other way, it had to pass through a two-litre bottle, B, which was almost completely filled with a solution of sulphurous acid. A special experiment showed that the gas, as it came out of the sulphurous acid bottle, contained 3·16 m.grms. of $SO_2$ per litre.

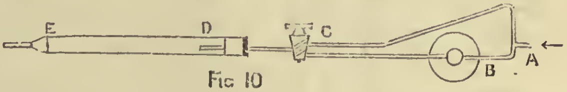

Fig. 10

In the experiment, the first step was to pass pure hydrogen over the red-hot reduced copper. A test-tube containing a quantity of acidulated water, coloured just perceptibly with permanganate, was then inserted between the outlet end of the reduced copper tube and the Pisani bottle, and seven litres of hydrogen, contaminated with $SO_2$ were passed through. The permanganate retained its colour, showing that no $SO_2$ got past the red-hot copper. In a subsequent experiment, the combustion tube was filled with oxide of copper, and an apparatus for the collection of the water formed inserted between the oxide of copper tube and the test-tube. As in the former case the reduction was started with pure hydrogen, impure hydrogen was then made to go through, and pure hydrogen again substituted for it at the end. About 50 grms. of oxide of copper were used, corresponding to 10 litres of hydrogen. The permanganate in the test-tube retained its colour, and the water collected as such was found free of sulphurous acid. This shows that neither copper nor oxide of copper allows any sulphurous acid to pass, or, in other words, that the sulphurous acid is decomposed completely with formation of sulphide of copper.

(To be continued).

## JEAN SERVAIS STAS.

It is a year since Science lost one of its most eminent representatives in the person of Jean Servais Stas. Six months before his death, when the Academy of Belgium celebrated the rare anniversary of fifty years of assiduous participation in his researches,—fifty years filled with the most persevering industry, the most remarkable discoveries,—Europe and America joined in hailing this great genius, this powerful and laborious investigator.

The researches of Stas on the atomic weights, on the laws of chemical proportions, on nicotine and the organic alkalies, on the constitution of matter, and on solar light, have placed him from the outset of his career and kept him up to its conclusion in the first rank among the masters of modern chemistry. As a superior analyst his works are of fundamental importance, and have supplied chemistry with foundations which cannot be shaken. By the extent of his researches, the profundity of his insight, the accuracy and the novelty of his methods, the works of Stas have become classical, and his name is inseparable from the very principles of Science.

This is not the limit of his fruitful influence. As Professor for twenty-five years at the Military School he has exercised a durable influence by his example and his advice. As a Commissioner of the Mint from 1865 to 1872 he brought this delicate function into exceptional prominence by the moral authority which in him was combined with the scientific spirit in so high a degree. The services which he rendered to the superior Sanitary Council, to the Central Statistical Commission, to University education, to the State Agricultural Laboratories, to the National Bank, and to various important branches of industry are not forgotten. At the Conference on the Metre and at the International Committees of Weights and Measures the activity of Stas was not less important, and the conclusions of his prolonged researches are now part and parcel of public law in most civilised nations.

It would be superfluous to insist on his great and manifold merits; they have been admitted at their full value by the unanimous testimony of the most eminent *savants* of our epoch.

The man, we must remember, was always on a level with his work. Nobility of soul, firmness of convictions, disinterestedness carried to the length of self-sacrifice, extreme simplicity of life, affectionate devotion to his friends, his colleagues, his pupils, to everyone who sought his advice or his support,—these were the universally known features of the moral character of Stas.

The memory of such a man cannot be too much honoured. The true monument is his works. Unfortunately, copies of the works of Stas have become scarce. The first duty which his friends and admirers seek to fulfil towards him is to secure the perpetuity of his works by a wide circulation. A new edition, grouping his memoirs, notes, and reports, scattered in fifty volumes, and reproducing them in a more convenient form, is a necessary enterprise.

A commemorative monument will complete this homage, and will recall a life entirely devoted to Science and to the public good.

In order to accumulate the resources—relatively considerable—which will be necessary to raise such a monument, and to re-edit the works of Stas, we make a warm appeal for the assistance of all who are interested in the progress of Science and of mankind.

Adhesions and subscriptions will be received by M. L. Errera, 1, Place Stephanie, Brussels.

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## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, January 19th, 1893.*

Prof. A. Crum Brown, President, in the Chair.

(Concluded from p. 82).

101. "*Salts of Active and Inactive Glyceric Acid; the Influence of Metals on the Specific Rotatory Power of Active Acids.*" By Percy F. Frankland, F.R.S., and J. R. Appleyard.

The authors have prepared and analysed a number of salts both of ordinary glyceric acid and of the dextrorotatory variety previously described by P. F. Frankland and Frew (*C. S. Trans.*, 1891, 96); the solubilities of many of them, and also the specific rotatory power in the case of the active salts, have been ascertained. The composition and solubilities of the corresponding salts are contrasted.

The specific rotatory powers of the several salts, determined in solutions containing about 10 per cent, are recorded in the following table, together with the molecular rotations of the salts and the calculated specific rotation of the glyceric acid corresponding to each salt.

The authors point out that the variations in the values for the specific rotation of the glyceric acid according to the different metals present in the salt. These values may be represented in round numbers, as unity in the case of the acid potassium salt, 1·5 in the case of the salts of the alkaline earths, 2 in that of the salts of the alkalis, magnesium, and cadmium, and 3 in the case of

| Salt. | Specific rotation, $[\alpha]_D$. | Molecular rotation, $\frac{M \times [\alpha]_D}{100} = [M]_D$. | Equivalent specific rotation of glyceric acid, $C_3H_6O_4$. |
|---|---|---|---|
| $Li(C_3H_5O_4)$ .. .. .. .. .. | −20·66° | −23·14° | −21·83° |
| $Na(C_3H_5O_4)$ .. .. .. .. .. | −16·13 | −20·65 | −19·48 |
| $K(C_3H_5O_4)$ .. .. .. .. .. | −16·46 | −23·70 | −22·36 |
| $K(C_3H_5O_4)(C_3H_6O_4)$ .. .. .. | − 9·24 | −23·10 | −10·90 |
| $NH_4(C_3H_5O_4)$ .. .. .. .. | −18·05 | −22·20 | −20·94 |
| $Ca(C_3H_5O_4)_2$ .. .. .. .. | −13·34 | −33·35 | −15·73 |
| $Sr(C_3H_5O_4)_2$.. .. .. .. .. | −11·91 | −35·44 | −16·72 |
| $Ba(C_3H_5O_4)_2$ . .. .. .. .. | −10·01 | −34·73 | −16·38 |
| $Mg(C_3H_5O_4)_2$ . .. .. .. .. | −20·08 | −46·99 | −22·16 |
| $Zn(C_3H_5O_4)_2$ . .. .. .. .. | −23·63 | −65·05 | −30·69 |
| $Cd(C_3H_5O_4)_2$ . .. .. .. .. | −15·29 | −49·23 | −23·22 |

the zinc salt. They compare these results with those which have been obtained by other observers in the case of other active acids and which have led to the generally accepted doctrine that the activity of an acid is influenced by the nature of the metal introduced in forming the salt. This doctrine is founded on the observations of Hoppe-Seyler on cholalic acid, of Oudemans on podocarpic and quinic acids, of Hartmann on camphoric acid, and of Landolt on tartaric acid. The authors, however, call attention to the fundamental optical difference between most of these acids and glyceric acid: thus the rotation of the glycerates is both opposite in sign and much greater in degree than that of the acid, whilst, on the contrary, cholalic and camphoric acids have a greater rotation than may be deduced from their salts; and podocarpic acid again has practically the same rotation as may be calculated from its salts. Quinic acid, however, has a somewhat higher rotation than that deducible from its salts, and the same relationships between the rotations of the quinates subsist in miniature as are exhibited on an exaggerated scale by the glycerates; zinc quinate having a distinctly higher, and barium quinate a distinctly lower, rotation than that of the other quinates. In the case of tartaric acid, again, a much higher rotation may be deduced from its salts than is shown by the acid, but the salts of tartaric acid which have been examined for rotation are just those in which only comparatively insignificant differences are observable in the case of the glycerates, viz., the salts of the alkaline metals and magnesium; on the other hand, the excessively high rotation of tartar emetic shows that the antimonyl group, at any rate, has a most important influence in affecting the rotation of the acid. In the case of lactic acid, however, there is the fullest analogy to glyceric acid, the rotation of the lactates being both opposite in sign and much greater in degree than that of the acid, the ratio of the rotation in the zinc salt to that in the calcium salt (the only two lactates which have had their rotation determined) being also almost identical for lactic and glyceric acid, being 1·805 and 1·951 respectively.

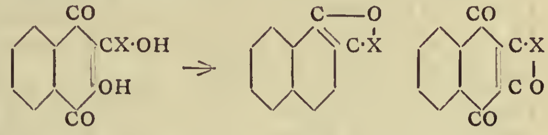
Before drawing any conclusions from these remarkable apparent relationships, the authors intend making a more detailed investigation of the rotations of these and other salts in solutions of different concentration. The results, however, as far as they go, appear to lend support and to extend the views on multiple rotation which have been expressed by Mulder (*Chem. Zeit.*, 1868, 58), Krecke (*J. Pr. Chem.*, v., 1872, 6), Landolt (*Ber.*, vi., 1873, 1073), and M. Thomsen (*Ber.*, 1880, 2168, 2264, 2269; 1881, 29, 134, 203, 807, 1647), but subsequently controverted by Landolt (*Ber.*, 1881, 296, 1048) and Oudemans (*Rec. Trav. Chim.*, 1885).

102. "*Dibromo-β-lapachone.*" By SAMUEL C. HOOKER and A. D. GRAY.

Dibromo-β-lapachone was first obtained in very small quantity as a secondary product in the preparation of bromo-β-lapachone (*cf. Trans.*, 1892, 640); although it was formed in the preparation of bromo-β-lapachone from lapachol, it was, nevertheless, impossible to produce it from bromine and pure bromo-β-lapachone. It is now shown that hydrogen bromide plays an important part in the conversion of the mono- into the di-bromo-derivative, an unstable additive compound of the former with bromine and hydrogen bromide being produced, which slowly passes into dibromo-β-lapachone. A number of derivatives prepared from dibromo-β-lapachone are described.

103. "*The Conversion of Para- into Ortho-quinone Derivatives.*" By SAMUEL C. HOOKER.

The author announces that he will subsequently adduce experimental evidence showing that, both in the lapachol and other groups, compounds derived from α-naphthaquinone, of the type represented by formula I., are far more readily converted by the action of acids into anhydrides derived from β-naphthaquinone (II.) than, as might, perhaps, have been expected, into anhydrides of the α-quinone type (III.).



I. II. III.

Thus, the benzal-dis-hydroxy-α-naphthaquinone of Zincke and Thelen (*Ber.*, xxi., 2203) is quantitatively converted into an anhydride derived from the β-quinone. A variety of similar compounds, derived from aldehyds other than benzaldehyds, have been prepared.

It will also be shown that, as in the case of the β-lapachones, the converse change of β-quinone anhydrides into α-quinone derivatives is easily effected by boiling with dilute solutions of caustic alkali. It is proposed to extend the experiments to hydroxyquinones generally.

104. "*The Nitro derivatives of Phenolphthalein.*" By JOHN A. HALL, M.Sc.

The author calls attention to the previous incidental references to nitro-derivatives of phenolphthalein by Baeyer (*Annalen*, ccii., 73), Frande (*Ibid.*, p. 154), and O. Fischer (*Ibid.*, ccvi., 99).

As a pure dinitro-derivative was not obtained by nitrating a sulphuric acid solution, phenolphthalein was dissolved in ten times its weight of acetic acid; a mixture of nitric acid and acetic acid was slowly added to the solution, keeping the temperature below 10°; 2 mols. of nitric acid were required by each mol. of phenolphthalein. After a time, a considerable quantity of yellow needles separated, which, after repeated re-crystallisations, melted constantly at 196°. A nitrogen determination gave 6·91 per cent; that calculated for dinitrophenolphthalein, $C_{10}H_{12}O_8N_2$, is 6·86 per cent.

Dinitrophenolphthalein forms yellow needles, fairly soluble in acetic acid and alcohol; it dissolves in alkalis with a yellow colour, but has practically no affinity for animal fibres. On reduction with sodium sulphide, it yields a fine blue solution, which, however, is very unstable. Frande states that, on reduction, his dinitrocresolphthalein yielded a blue solution, from which he isolated an amido-compound, but apparently did not analyse it. Some attempts were made to condense phthalic anhydride, and ortho- or para-nitrophenol, but without success.

*Tetranitrophenolphthalein.*—Phenolphthalein dissolved in five times its weight of sulphuric acid was nitrated with 2 mol. proportions of nitric acid at about 10°; the mixture was allowed to stand about two hours, and its temperature was then raised to from 20° to 30°, and kept between these limits during the addition of another equal weight of nitric acid; as this second part of the nitration did not seem to proceed so rapidly as the first, the mixture was allowed to stand twelve hours, then poured into a large volume of water: the nitro-compound separated as a white precipitate, which was filtered and washed till free from sulphuric acid. The dried product proved to contain about 75 per cent of a substance soluble in cold acetic acid to the extent of only about 1 per cent, which, by repeated re-crystallisations from acetic acid or a mixture of phenol and alcohol, was obtained of a constant melting point (244—245°). A nitrogen determination gave 10·89 per cent; that calculated for tetranitrophenolphthalein, $C_{20}H_{10}O_{12}N_4$, is 11·2.

Tetranitrophenolphthalein is difficultly soluble in most ordinary solvents; it forms pale yellow indistinct crystals, readily soluble in alkalis; salts of the heavy metals, as barium, lead, and silver, precipitate its neutral solution. The sodium salt is a yellow dye-stuff, sold under the name of aurotine.

On alkaline reduction it yields an unstable blue colour. It was also observed that when phenolphthaleinsulphonic acid (*Annalen*, ccii., 73) was treated with 2 mol. proportions of nitric acid in presence of sulphuric acid, it yielded a soluble nitrosulphonic acid, but when 4 mol. proportions of nitric acid were used and the temperature was allowed to rise to 30° C., the product was for the most part insoluble in water and consisted simply of impure tetranitrophenolphthalein.

The author thanks Mr. F. Moore, B.Sc., for the analytical figures which are quoted, and Dr. Dreyfus, Managing Director of the Clayton Aniline Company, where the experiments were made, for permission to publish the results.

105. "*A Method for the Preparation of Acetylene.*" By Morris W. Travers.

Maquenne has recently published (*Compt. Rend.*, 1892) an account of a method of preparing acetylene by the interaction of water and barium carbide, the carbide being made by reducing barium carbonate with magnesium in the presence of carbon, a method which affords about half the calculated quantity of barium carbide. Wöhler obtained calcium carbide by heating calcium-zinc alloy with carbon in a graphite crucible.

Calcium carbide may be prepared in quantity by reducing calcium chloride with sodium in the presence of carbon. The operation is conducted as follows:—45 grms. of sodium are placed at the bottom of a deep iron bottle, and an intimate mixture of powdered gas carbon and calcium chloride which has been well dried on a hot iron dish is then introduced; the top of the bottle, furnished with a long neck, having been screwed on, the bottle is heated to bright redness during half an hour; it is then removed from the fire, stoppered, and cooled with water. When broken away from the bottle, the product is dark grey in colour and consists of sodium chloride, calcium carbide, and the excess of carbon added to render the mass less compact; usually about 16 per cent of carbide is formed, which is half the theoretical quantity. In practice, 1 grm. of sodium thus converted into carbide is found to yield 240 c.c. of acetylene instead of 487 c.c. the calculated equivalent quantity.

## PHYSICAL SOCIETY.

*Annual General Meeting, February 10th, 1893.*

Walter Baily, M.A., Vice-President, in the Chair.

The reports of the Council and Treasurer were read and approved, copies of the balance sheet being distributed to members. From the former it appears that the Society now numbers 371 ordinary members and twelve honorary members, and during the past year the Society has lost six members by death, viz., the Rev. T. Pelham Dale, Dr. J. T. Hurst, B. Loewy, C. E. Walduck, G. M. Whipple, and P. W. Willans. Obituary notices accompany the report.

The Treasurer's statement shows the financial condition of the Society to be satisfactory.

A cordial vote of thanks to the Committee of Council on Education for the use of the rooms and apparatus of the Royal College of Science was proposed by Mr. Shelford Bidwell, seconded by Mr. Blakesley, and carried unanimously. A similar vote was accorded to the auditors, Mr. H. M. Elder and Mr. A. P. Trotter, on the motion of Dr. Gladstone, seconded by Prof. S. P. Thompson. Prof. Ramsay proposed a vote of thanks to the Officers of the Society for their services during the past year; this was seconded by Prof. Fuller and carried. Prof. Perry responded.

The following gentlemen were declared duly elected to form the new Council:—

*President*—Prof. A W. Rücker, M.A., F.R.S.

*Vice-Presidents*—Walter Baily, M.A., Major-General E. R. Festing, R.E., F.R.S., Prof. J. Perry, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S.

*Secretaries*—H. M. Elder, M.A., 50, City Road, E.C., and T. H. Blakesley, M.A., M.Inst.C.E., 3, Eliot Hill, Lewisham, S.E.

*Treasurer*—Dr. E. Atkinson, Portesbery Hill, Camberley, Surrey.

*Demonstrator*—C. Vernon Boys, F.R.S., Physical Laboratory, South Kensington.

*Other Members of Council*—Shelford Bidwell, M.A., LL.B., F.R.S., W. E. Sumpner, D.Sc., Prof. G. Fuller, J. Swinburne, Prof. J. V. Jones, M.A., Rev. F. J. Smith, M.A., Prof. G. M. Minchin, M.A., L. Fletcher, M.A., F.R.S., Prof. O. Henrici, Ph.D., F.R.S., James Wimshurst.

In response to invitations for suggestions regarding the working of the Society, Prof. S. P. Thompson said all must appreciate the efforts of the late Council, and particularly of the honorary secretaries, in making the Society better known. But he could not help thinking that there were many persons among teachers of physics and scientific amateurs whose active sympathies it was desirable to engage, who were not yet associated with the Society. Perhaps the time of meeting was not convenient for all, but he thought much might be done by freely circulating particulars of what was going on at the meetings. The daily papers merely announced the meetings, but said nothing as to the place of meeting or the papers to be read. In his opinion the Society did not take the position in the scientific world to which it was entitled, and he wished to inspire members with a determination to bring its claims prominently forward.

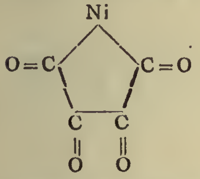
Mr. Blakesley pointed out that almost all the scientific and technical papers gave full announcements of the meetings and of the papers to be read.

Mr. W. F. Stanley said Friday afternoon was not convenient for scientific men engaged in trade.

The meeting was then resolved into an Ordinary Science Meeting, and Mr. C. E. Grove was elected a member of the Society.

Dr. J. H. Gladstone, F.R.S., read a paper on "*Some Recent Determinations of Molecular Refraction and Dispersion.*"

The paper relates to the new metallic carbonyls, the metals indium and gallium, sulphur, and to liquefied oxygen, nitrous oxide, and ethylene. The carbonyls were found to be extremely refractive and enormously dispersive. For iron pentacarbonyl, $Fe(CO)_5$, the molecular refraction for the line $\alpha$ of hydrogen was found to be about 68·5, and the molecular dispersion between $\gamma$ and $\alpha$ of hydrogen 6·6. For nickel tetracarbonyl, $Ni(CO)_4$, the corresponding numbers are 57·7 and 5·93. In discussing the results it was pointed out that if the molecular refraction of CO be taken as 8·4, the value expected in organic substances, then the atomic dispersion of nickel and iron come out greatly in excess of the known values as determined from solutions of their salts. The author considers the most probable explanation of the excessive refractions and dispersions of the carbonyls is to be sought in the peculiar arrangement of the CO, and on optical as well as chemical grounds accepts the ring formulæ indicated by Mr. Mond in his lecture at the Royal Institution, viz. :—



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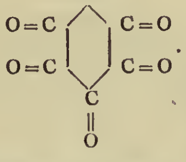

On this supposition the molecular refraction of CO comes out 11·9 from the nickel compound and 11·3 from the iron ore, whilst the molecular dispersion ($\gamma - \alpha$) is about 1·3 in each case. For indium and gallium the atomic refractions, calculated from latest data, are 13·7 and 11·6 respectively. Sulphur has been examined in the states of solid, liquid, and gas, and also in simple chemical combination, and in solution, all the resulting numbers for its atomic refraction being remarkably concordant. For the line C this is about 16. The dispersions in all the different states are also in close agreement. Numbers relating to carbon and chlorine are also given.

The specific refractions of oxygen, nitrous oxygen, and ethylene in the liquid states had been recently determined by Profs. Liveing and Dewar. For liquid oxygen the refraction equivalent (3·182) differs little from that deduced from gaseous oxygen at ordinary temperatures (3·0316), and also corresponds fairly closely to the 3·0 obtained by Landolt from organic compounds. Liquid nitrous oxide gave 11·418 and 11·840 as the molecular refractions for the red ray of lithium and the line G respectively. In discussing these numbers it was pointed out that nitrogen in nitrous oxide was not in the same condition as nitrogen in ammonia. The latest determinations with liquid ethylene gave the molecular refraction for the line A as 17·41, the theoretical value being 17·40, thus showing very close agreement.

Mr. E. C. C. **Baly** made a communication on "*Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge.*"

On examining with a spectroscope a vacuum tube, containing a small quantity of hydrogen, the author noticed that the hydrogen lines were strongly visible in the negative glow, but could not be seen in the body of the tube. This observation was confirmed by examining other tubes, and seemed to point to a separation of gases in the tube. From subsequent experiments it also appeared that the striæ were due to this separation. By using a double tube containing a mixture of carbon dioxide and hydrogen, whose parts were connected by a narrow neck which could be sealed, and the parts detached, the gases were fractionated by the discharge. After sealing off, the spectra of the two parts were examined; the one that had formed the positive pole showed only a trace of hydrogen, whilst the other showed it brilliantly. Other mixtures gave similar results, and the separation was found not to depend on the relative molecular weights of the gases. A very close connection between separation and striæ was noticed, the two phenomena always occurring together. On using a tube with a very minute negative electrode to avoid the negative glow, neither striation nor separation took place, but on reversing the current so as to make the large electrode the negative one, both phenomena became well marked. If the author's views were correct a pure vapour or gas should not striate. Pure mercury vapour gave no striæ, but on allowing a small quantity of other gas to pass into the tube they at once appeared. Pure vapours of iodine, sulphur, arsenic, and mercuric iodide gave similar results. Attempts to prepare a tube containing pure hydrogen which should not striate were not perfectly successful, but the striations usually seen in hydrogen tubes were reduced so as to be barely distinguishable. The author therefore concludes: 1. When an electric current is passed through a rarefied mixture of two gases, one is separated from the other and appears in the negative glow. 2. That striæ are caused by the separation of the two gases, and do not occur in a single pure gas or vapour.

Mr. **Blakesley** read a communication from Dr. W. Crookes relating to Mr. Baly's paper, and pointing out that in his Presidential Address to the Institution of Electrical Engineers in January, 1891, he had given reason for believing stratification due to the gas not being homogeneous. He had also shown that the character of the stratification depended on the potential of the discharges.

Prof. **Ramsay** said no proof had been given that electrolysis occurred in such tubes, and it was an open question whether molecules would convey electricity as ions do. So far as was seen, no ions existed in vacuum tubes. Possibly the stratifications resulted from collisions of molecules giving higher temperatures at some parts of the tube; but this was doubtful.

Mr. **Enright** thought the analogy with electrolysis was not quite clear, for in a mixture of simple gases the elements were not combined chemically, and electrolysis involved the splitting up of chemical compounds.

Prof. S. P. **Thompson** hoped the author would continue his important work and clear up the doubtful points in vacuum tube phenomena. Some difficulty existed in classifying the separation of the gases with electrolysis; for in the latter, the effects were only visible at the electrodes and not in intermediate portions of the substance. The question whether vacuum tube discharges were strictly analogous might be tried by fractionating through more complicated tubes. Prof. Schuster has considered the analogies in his Bakerian Lecture, and published some important results, some of which tended to show that wandering ions existed in vacuum tubes through which discharges were being passed.

Referring to Prof. Ramsay's remarks about molecules not carrying electricity, he (Prof. Thompson) said that electric winds were phenomena which pointed to the opposite conclusion. Similar convective action also occurred in turpentine and other insulating liquids. He wished to know whether the author had tried if a low voltage (say 100 volts) applied for a long time to a vacuum tube, would produce separation of the contained gases. Porret's phenomenon of electric osmose seemed to have some bearing on the subject, as also Faraday's observations on the movements of scraps of silk in turpentine, and showing that in non-conducting liquids there were phenomena somewhat analogous to electrolysis.

Prof. **Ramsay** said that if indigo be put in a poor conductor, such as distilled water, and the mixture subjected to electrolysis, all the blue colour became concentrated about one electrode, whilst if arsenic sulphide be similarly treated, the colour went to the other pole. On mixing the two solutions, all coagulates and goes down. He could give no explanation of these remarkable effects.

Mr. **Blakesley** inquired whether tubes which had been kept some time showed the same phenomena as immediately after sealing.

In his reply Mr. Baly said the striæ in some tubes had very peculiar shapes, some showing discs and others showing cones alternately base to base and apex to apex. He had tried the experiment with complicated tubes as suggested by Prof. Thompson, but the result was not conclusive.

## CORRESPONDENCE.

### THE ETHICS OF "ABSTRACTION."

*To the Editor of the Chemical News.*

Sir,—There is an abstract of a paper read by Mr. E. Lodge before the Society of Dyers and Colorists in the number of the *Jour. Soc. Chem. Ind.* for July, 1892, and this abstract concludes with the remark: "Several of the author's statements are at variance with the results of other experimenters and require confirmation." I should like to draw attention to two points raised by a study of this sentence—its construction and its origin.

In the first place, it seems to me that we have not to consider the author's "statements," but the results of the author's experiments with regard to the results of other experimenters. In the second place, the other experimenters should be named in order that the student or technologist may have an opportunity of examining the question for himself. In the third place, it does not appear to be absolutely correct to assume that Mr. Lodge's results require confirmation, it would be more fair to say that a revision of the work on the subject in question is necessary.

The abstract conveys no clue as to the origin of the remark with which it concludes. It may have its origin from one of three sources. Mr. Lodge may have remarked that his results differed from those obtained by others; a discussion following the paper may have brought something to light with regard to the results of other experimenters; or the abstractor himself may have added the remark on his own responsibility. In any of these cases the abstract should carry with it an indication whereby the value of the practically adverse criticism may be determined.—I am, &c.,

"Dyer."

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—The proposal to erase the letters F.C.S. from the Register of the Institute of Chemistry will surely be regarded by most persons as a slight upon the older parent Society, and this in spite of all disclaimers of any such intention.

May we not hope that on reflection the Institute will resume its filial relation to the Chemical Society by rescinding the resolution?—I am, &c.,

G. A. Keyworth.

Hastings, Feb. 20, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 6, February 6, 1893.

**Preparation of Carbon under a Strong Pressure.**—Henri Moissan.—The author refers the varieties of carbon to three chief types: diamond, graphite, and amorphous carbon, and he lays before the Academy an account of the preparation of carbons of a high specific gravity. As a preliminary he has studied the composition of the ash, of the diamond, of bort, and of carbonado. He shows the existence of graphite, of carbonado, and of microscopic diamonds in the "blue earth" of South Africa, and the existence of the diamond in the meteorite of Cañon Diablo. He has studied the solubility of carbon in magnesium, aluminium, manganese, chrome, uranium, silver, platinum, and silicon. Operating on a mixture of diamond, graphite, and amorphous carbon he has removed all matter except diamond by successive treatment with hydrochloric or nitric acid, boiling sulphuric acid, hydrofluoric acid, and a mixture of potassium chlorate with nitric acid. He succeeds by these means in separating from the "blue earth" a variety of carbon hard enough to scratch ruby, and of the specific gravity of diamond. It burns in oxygen, yielding 3—3·5 carbonic acid.

**Reproduction of the Diamond.**—C. Friedel.—A discussion on the foregoing paper.

**Study of the Chromium Fluorides.**—C. Poulenc.—The author has obtained anhydrous and crystalline chromium mono- and sesquifluorides. He also describes a new hydrated chromium fluoride, $Cr_2F_6,7H_2O$, and a new method of preparing the double potassium-chromium fluoride, $Cr_2F_6,6KF$.

**New Process of Soldering for Aluminium and various Other Metals.**—J. Novel.—Aluminium is soldered with the alloy given below, with the ordinary tinman's soldering iron, or with the blowpipe. It does not oxidise or discolour the metal. The following solders are employed for aluminium:—No. 1. Pure tin; melts at 250°. No. 2. Pure tin 1000 parts; fine lead 50 parts. Melts at from 280° to 300°. No. 3. Pure tin 1000 parts; pure zinc 50 parts. Melts at from 280° to 300°. These three solders may be used in the manufacture of aluminium trinkets. For the following two solders the soldering iron should be made of pure nickel. No. 4. Pure tin 1000 parts; pure copper 10 to 15 parts. Melts at from 350° to 450°. No. 5. Pure tin 1000 parts; pure nickel 15 parts. Melts at from 350° to 450°. No. 6. Pure tin 900 parts; pure copper 100 parts; bismuth 2 to 3 parts. Melts at from 350° to 450°, and is recommended for soldering aluminium bronze.

**Action of Acetic Acid and Formic Acid upon Turpentine.**—MM. Bouchardat and Oliviero.—For this paper we refer to the original.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. vii., No. 83.

**Experiments in the Filtration of Sewage performed by the Sanitary Council of the State of Massachusetts.**—(Taken from the *Journal of the Franklin Institute*).—The only novelty in these experiments, which are described as very successful, consists in the sewage being run in so gradually that the beds were never entirely submerged. No analyses are quoted.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 1.

**Source of Error in the Ultimate Analysis of Organic Compounds, especially Nitrogenous.**—G. Neumann.—As various authors allege—among others A. Léduc—ignited copper can absorb hydrogen. The author has observed this behaviour, but he has not been able to verify the statement of Thudichum and Hake and of Vortmann that carbon dioxide, if passed over ignited copper which has been reduced with hydrogen, is capable of expelling all the hydrogen. On the contrary, he proves that besides the retention of a part of the hydrogen on subjecting the copper to a current of carbon dioxide, there occurs an absorption of carbon dioxide.

**Modification of the Dumas's Method for the Determination of Nitrogen.**—F. Blau (*Monats'hefte fur Chemie*).—This paper requires the two accompanying figures.

**Specific Gravity of Acetone, Its Solvent Power for Certain Inorganic Salts, and Its Solubility in Aqueous Solutions of Sugar.**—W. H. Krug and Mc Elroy.—(From the *Jour. Anal. Chem.*).

**Separation of Salicylic and Benzoic Acids.**—J. Schaap (*Ned Tyds. Pharm.*).—Already inserted.

**Reverdin and De la Harpe's Method for Determining Aniline and Monomethylaniline.**—M. Giraud.—A mixture of acetic anhydride and dimethylaniline kept in well closed vessels remains for a week without decomposition.

**Determination of the Acidity of Wine derived from Fixed and Volatile Acids.**—J. A. Müller.—This paper will be inserted in full.

**The Detection of Cherry Juice in Raspberry.**—Wimmer (*Pharm. Zeit.*).—The author adds basic lead acetate and filters. If a few per cents of cherry juice are present, the filtrate is blue with a reddish reflection. Pure raspberry juice, if similarly treated, yields a filtrate which is nearly colourless. The author finds that this test must be applied with much caution and in presence of pure comparative samples.

**Pure Culture of Motile Bacteria.**—R. Kluge and G. Marpmann.

**Diagnosis of the Typhus Bacillus.**—J. Weyland.

**Staining the Bacilli of Tubercle.** — Neumann-Wender.—These three papers will be inserted in full.

**Sophistication of Butter.**—H. W. Wiley.—(From the *Jour. Anal. Chemie*).

**Analysis of Cheese.**—Arnoldo Maggiora (*Archiv. fur Hygiene*).—The author determines moisture, fat, by extracting the dry residue with petroleum ether in Soxhlet's apparatus, crude proteine, determining nitrogen by the Kjeldahl process and multiplying by 6·25; pure proteine, separating the albumenoid substances by Stutzer's process, and determining its nitrogen by the Kjeldahl process, multiplying finally by 6·25; ammoniacal nitrogen, amido-nitrogen, and ash.

**Advances in the Fat, Oil, Soap, and Naphtha Industries.**—D. Holde (*Chem. Zeit.*).—A pure compilation.

**Examination of Wool-Fat (Lanoline).**—H. Helbing and F. W. Passmore.—The authors saponify by covering 5·3 grm. anhydrous wool-fat with 20 c.c. alcoholic potassa-lye in a strong flask containing about 50 c.c., stoppering and heating for two hours to 100° with occasional agitation.

**Detection of Resin-Size in Paper.**—W. Harrberg (*Chem. Zeit.*).—A piece of the paper is laid over a hollow support (a tumbler), and about four to six drops of ether are let fall upon the middle of the leaf. If resin is present a resinous border will appear after the ether has evaporated.

**Valuation of Indigo.**—A. Müller (*Chem. Zeitung*).—The author stirs up 0·5 grm. of the sample in the finest powder with 10 grms. sulphuric monohydrate (obtained by mixing seven parts of sulphuric acid at 95·5 per cent with three parts of fuming sulphuric acid containing 30 per cent of sulphuric anhydride), converts it into the disulpho-salt by means of heat, dilutes it when the reaction is completed to 1 litre, and titrates with permanganate in the usual manner until the olive tone of the liquid has disappeared.

**Determination of the Fineness of Powdered Sulphur.**—Chancel (*Weinlaute*).—For this paper we must refer to the original.

## MEETINGS FOR THE WEEK.

Monday, 27th.—Medical, 8.30.

Tuesday, 28th.—Institute of Civil Engineers, 8.
— Photographic, 8.
— Royal Medical and Chirurgical, 8.30.
— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
— Society of Arts, 8. "Russia as a Field for Tourists," by Sir Edward Braddon, K.C.M.G.

Wednesday, March 1st.—Society of Arts, 8. "Tele-Photography," by Thomas R. Dallmeyer.

Thursday, 2nd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Factors of Organic Evolution," by Prof. Patrick Geddes.
— Chemical, 8. "Notes on Optical Properties as Indicative of Structure" (postponed), by H. E. Armstrong. "The Ethereal Salts of Active and Inactive Glyceric Acid," by P. Frankland and J. MacGregor. "Limits of Accuracy of Gold-bullion Assay, and the Losses of Gold Incidental to it — The Volatilisation of Gold," by T. R. Rose. "The Interaction of Alkali-cellulose and Carbon Disulphide—Cellulose Thiocarbonates," by C. F. Cross, E. J. Bevan, and C. Beadle. "A New Atomic Diagram and Periodic Table of the Elements."

Friday, 3rd.—Royal Institution, 9. "Sculpture, considered apart from Archæology," by George Simonds.
— Geologists' Association, 8.
— Quekett Club, 8.

Saturday, 4th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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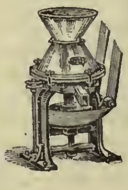

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THE CHEMICAL NEWS.
Vol. LXVII., No. 1736.

## A SOURCE OF ERROR IN THE ULTIMATE ANALYSIS OF ORGANIC SUBSTANCES.

By G. STILLINGFLEET JOHNSON.

It is gratifying to me to find that some work which I did seventeen years ago is receiving confirmation in Germany. In the *Zeit. Anal. Chemie* (vol. xxxii., Part 1) G. Neumann comes to the conclusion that hydrogen gas, occluded in copper turnings, is a source of error on the side of excess in hydrogen determinations.

In the *Chem. Soc. Jour.* (1876, i., 178), I first published a notice of this source of error, and in the same journal (May, 1879) I followed it up with a second paper "On the Occlusion of Hydrogen by Copper." In this second paper the following facts were proved.

1. Metallic copper occludes very varying quantities of hydrogen, according to the state of its surface.
2. Alternate oxidation and reduction of the same copper tends gradually to diminish the weight of occluded hydrogen.
3. Copper, which has occluded hydrogen, parts with its occluded gas when heated to redness in pure nitrogen.
4. Copper, which has occluded hydrogen, does not part with its occluded gas when heated to redness *in vacuo*.
5. Perfectly pure copper occludes no hydrogen whatever. The presence of *sulphur* appears to increase occlusion.
6. A good test for occluded hydrogen in copper is to boil the metal with solution of potassium chlorate, which is reduced to chloride.

It may be interesting to indicate the general method of procedure which I at present adopt to avoid this error.

(1) The copper employed is selected as *free from sulphur* as possible.

(2) The copper is oxidised and reduced alternately several times before using.

(3) The substance is burnt in a boat, behind which is a second boat containing reduced copper, and a third boat containing fused $KClO_3$. In front of the boat with the substance is granulated copper oxide, and in front of that the reduced copper for reduction of the oxides of nitrogen.

The whole tube is now heated to redness, except the portions occupied by the boats containing the $KClO_3$ and the substance to be burned, and a slow stream of dried air is passed through until all the reduced copper behind the substance has been oxidised. The weighed apparatus is then adjusted in front and the combustion proceeded with. My hydrogen determinations are (with the above precautions) usually within 0·1 per cent of the theory.

King's College, London, Feb. 20, 1893.

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## THE SOLUTION OF AIR IN SEA-WATER.

By A. E. RICHARDSON, B.A., F.C.S., A.M.I.E.E.

It is a well-known fact that the amount of gas capable of being held in solution by a given liquid is directly proportional to the pressure exerted, unless chemical combination takes place between the gas and the solvent. But the pressure at any point within a fluid, which is incapable of being compressed, is proportional to the depth of that point below the surface of the fluid. Consequently, it is obvious that the water deep down in the ocean must be capable of dissolving greater quantities of air than water at the surface.

To illustrate this point, let us take an extreme case and roughly calculate the volume of air which could be absorbed by unit volume of water deep down in the sea. The depth of the Pacific Ocean is known to be as much as 40,000 feet (or 7½ miles) in at least one place.

First, we will calculate the pressure exerted upon a cubic foot of water at that depth. Assuming that the specific gravity of sea-water is roughly 1·026, a cubic foot of sea-water will weigh 1026 ozs. (a cubic foot of distilled water is generally taken as weighing 1000 ozs.). Then the pressure exerted per square foot at a depth of 40,000 feet will be—

$$40{,}000 \times 1026 \text{ ozs.} = 40{,}000 \times \frac{1{\cdot}026}{16} \text{ lbs.}$$

Hence the pressure per square inch will amount to—

$$\frac{40{,}000}{144} \times \frac{1026}{16} = 17{,}812\tfrac{1}{2} \text{ lbs.}$$

The pressure due to one atmosphere may be roughly taken as 15 lbs. per square inch. Thus the pressure at a depth of 40,000 feet is equivalent to that of 1187 atmospheres. This, with the pressure due to the air above, amounts to 1188 atmospheres.

It must be borne in mind that this is only an approximate calculation. For instance, the density of sea-water is taken at a rather low figure, and no allowance is made for the compressibility of sea-water under great pressures.

Accepting, however, 1188 atmospheres as the approximate pressure at the stated depth, let us calculate the volume of air which a unit volume of the water would be capable of dissolving under this pressure.

I have no data at hand for the absorption coefficients of sea-water for oxygen and nitrogen or for air, so I will take the coefficients for pure water. Here again an error will arise, for sea-water cannot absorb so much air as ordinary water; for it has been found that in solutions of different substances the solubility of gases is in most cases diminished.

One volume of water at normal temperature and pressure absorbs about 0·0245 volume of air. With the temperature remaining constant the volume of gas absorbed remains the same under all pressures. But this volume of air, under a pressure of 1188 atmospheres, would occupy a volume of 0·0245 × 1188 under normal pressure. This quantity amounts to 29·106 volumes. Hence, a cubic foot of water at a depth of 40,000 feet is capable of absorbing 29 cubic feet of air measured at normal pressure.

Since a c.c. of air weighs 0·00129 grms. 29 c.c. will weigh 0·037 grm. That is to say, the water in question would be capable of dissolving about 1-27th of its own weight of air. Nor does there seem any reason to suppose that this amount of air is not absorbed, for the atmospheric gases must permeate the whole of the ocean's depth in order that deep sea fishes may obtain the oxygen necessary for the preservation of their existence. At a depth of 1380 feet water absorbs its own volume of air (measured at atmospheric pressure). Thus in all water below this depth there is dissolved more than its own volume of air. We have then a second but submerged atmosphere.

In this most marvellous submarine atmosphere are vast quantities of air stored away,—how vast it is difficult to estimate. Remembering that three-fourths of the face of the earth is covered by water, one is apt to conclude that there is almost as much air hidden away in the ocean's depth as is found above its surface. What effect such great pressures have upon the solvent powers of the water for solid constituents it is doubtful to say. Probably the solvent powers are much modified by the presence of such quantities of dissolved gases. It is possible that such considerations as the foregoing have already appeared in print. As, however, I have never read or heard of such suggestions, I venture to bring the question before your readers.

Dorking, Surrey.

## BEHAVIOUR OF THE GADOLINITE EARTHS WITH POTASSIUM CHROMATE.

By G. KRÜSS and A. LOOSE.

(Continued from p. 89).

### *Preparation of Didymium Oxide by Means of Potassium Chromate from a Mixture of the Gadolinite Earths.*

It was investigated whether and how quickly didymium oxide could be obtained by repeated precipitation in the cold with potassium chromate. The institution of these experiments seemed interesting with reference to the renewed examination to which didymium has been submitted since its scission into neodymium and praseodymium.

For a preliminary experiment five different earthy mixtures were united, containing all the erbia and didymia earths (except yttria), and on determination of the equivalents showing the following values for $\overset{III}{R}$. 111·7, 113, 115·6, 120·9, and 135·5, in the mean =119·3. They were converted into a nitrate solution. After neutralising the excess of acid the liquid was precipitated with potassium chromate in the cold, and the earth contained in the precipitate was examined. It was a $\overset{III}{R}=133{\cdot}7$. It was converted into a nitric solution, with which the chromate precipitation was repeated. On determining the combining-weight, the material obtained was $\overset{III}{R}=137{\cdot}7$, and after again repeating the chromate treatment $\overset{III}{R}=142$, After these three operations the didymium spectrum had become considerably more intense.

This was an inducement to submit to the above method for preparing didymium oxide, a material which, beside small quantities of samarium and holmium, contained erbia, didymia, and yttria in approximately equal proportions. The nitrate solution of this material displayed the spectrum :—

| λ. | Strength of absorption. | Symbol. |
|---|---|---|
| 728·3.. .. .. | Very strong | Di$\alpha$ |
| 679·4.. .. .. | Faint | Di$\beta$ |
| 579·2.. .. .. | Very strong | Di$\gamma$ |
| 523·1.. .. .. | Strong | Er$\beta$ |
| 512·2.. .. .. | Fading | Di$\varepsilon$ |
| 482 .. .. .. | Distinct | Di$\zeta$ |
| 477·7.. .. .. | ,, | Sm$\beta$ |
| 469 .. .. .. | ,, | Di$\eta$ |
| 463·2.. .. .. | ,, | Sm$\beta$ |
| 445·1.. .. .. | Strong | Di$\delta$ |
| 428·5.. .. .. | Very distinct | X$\eta$ |

Hence it contained much erbium and didymium, and on determining its equivalent it was found to be $\overset{III}{R}=131{\cdot}5$. Much yttria is therefore present doubtless in a proportion approximately equal to the erbia and didymia, since—

$$\frac{(\overset{III}{Er}=166)+(\overset{III}{Di}=146)+(\overset{III}{Y}=90)}{3} = 134\ \overset{III}{R},$$

—a mean value which does not greatly differ from the value $\overset{III}{R}=131{\cdot}5$ as ascertained. This material was resolved into four fractions by precipitation in the cold with $K_2CrO_4$.

The first and the second fraction both gave on analysis a $\overset{III}{R}=146$, where the oxide before conversion into sulphate had been heated in a current of hydrogen until its weight was constant. The third fraction gave $\overset{III}{R}=138{\cdot}3$, and the fourth $\overset{III}{R}=126{\cdot}2$.

The first and second fraction had therefore given at once the former atomic weight for didymium, perhaps slightly too high. In the spectrum the Er$\alpha$ line was no longer visible, though the Er$\beta$ line was still present. These two fractions were combined and the chromate method was again applied, when the Er$\beta$ line appeared fainter and the didymium oxide showed on analysis $\overset{III}{R}=145{\cdot}3$.

We may consider the atomic weights hitherto found for didymium:—Marignac in 1853 made it 144; Hermann in 1860 142·44; Erk found it about 143, and Zschiesche 141·2, both in 1870; Cleve in 1874 found it 147·01, and Marignac in the same year from 143·6 to 144. Brauner in 1882 gave the value 146·58, which he afterwards rejected and adopted 145·52. Subsequently he split up the apparently purest didymium into earths, the atomic weights of which varied from 143·3 to 149·4. According to him the increases of the atomic weights were due to the presence of impurities of erbium, holmium, and samarium. Lastly, Auer von Welsbach on decomposing didymium found for praseodymium 143·6 and neodymium 140·8.

According to these results the atomic weight of didymium as found by the chromate method seems rather too high. The cause may easily be found in traces of samarium and erbium which adhere obstinately, but from which in case of need it may be purified by fractionated precipitation with ammonia. Otherwise the oxide obtained agreed well with the descriptions given for ordinary didymium oxide. It was of a dark brown colour as it was obtained by Mosander, Hermann, and Zschiesche. On reduction in a current of hydrogen the colour changed to a dirty pale grey. The excess of oxygen in the brown earth amounted in two determinations of pure specimens to 0·447 and 0·5 per cent. Hermann and also Marignac obtained an excess of 0·446, 0·32, and 0·88. Frerichs and Smith (*Liebig's Ann.*, 191) concluded that this excess was 7·13 per cent, but they were long ago refuted by Cleve, Nilson, and others. The sulphate of the oxide obtained by means of chromate generally appeared as a sintered cake of felted needles of a violet colour, resembling that of *Colchicum autumnale*. A borax bead was reddened by the oxide.*

We may also obtain very pure didymium oxide (in the ordinary sense of the word) from an earthy nitrate solution not too poor in didymium by a single precipitation with potassium chromate in the cold. If the earthy material contains but a scanty proportion of didymium, the earth can be isolated only by a treatment with chromate several times repeated.

Finally, to explain the reaction of potassium chromate and didymium nitrate, the following experiment was tried: As the didymium precipitate thrown down by $K_2CrO_4$, corresponding to the potassium didymium sulphate precipitate, might possibly consist of a potassium didymium chromate, about 0·3 grm. of neutral didymium sulphate was precipitated with a very concentrated solution of potassium chromate of a known strength, whereby the didymium was completely separated out. After making up the solution to 250 c.c., and allowing the precipitate to subside, 10 c.c. of the supernatant potassium chromate solution were taken out by means of a pipette. A determination of the potassium present showed that all the potassium used as chromate was present in the solution. Hence no formation of a double salt takes place.—*Zeit. für Anorganische Chemie*, vol. iii., p. 92.

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**Society of Arts.**—Prof. Chandler Roberts-Austen will commence a course of three Cantor Lectures on "Alloys" at the Society of Arts on Monday next, March 6, at 5 o'clock. The remaining lectures will be given on the two following Monday afternoons at the same hour.

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* "On the Interesting Property of Didymium Glass of Effecting an Absorption of Its Own Fluorescent Light." (See Lommel, *Ann. Phys.*, ii., 24).

# DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS.

By ADOLPHE CARNOT.

It is known that steels and irons of good quality can contain merely a very small proportion of phosphorus, and that a few ten-thousandths of that element suffice to modify greatly the properties of the metal. Hence the greatest importance is attached to an exact determination of the proportion of phosphorus.

Numerous methods have been proposed and give in different laboratories results which are often little accordant. The method which I am about to study, founded, like most others, on the use of ammonium molybdate, yields with less trouble more regular and more trustworthy results.

It differs from them (1) by the method of separation (and of determination) of the silicon, which is effected by means of sulphuric acid; (2) by the process for destroying the compounds of carbon in which chromic acid is employed; (3) by the nature of the final compound which is not magnesium pyrophosphate containing 27·928 per cent of phosphorus, but dried ammonium phosphomolybdate, which when obtained by a second precipitation under identical conditions presents a constant composition. It only contains 1·628 per cent of phosphorus, *i.e.*, seventeen times less than the pyrophosphate. Hence there is much greater accuracy in the determination.

We operate upon a portion of 5 grms. for irons, steels, and pure cast metal,—1 grm. or even 0·5 grm. being sufficient for phosphoriferous cast metals. The metal is treated with 40 c.c. of pure nitric acid in a large porcelain capsule, which is covered at once with an inverted funnel in order to avoid the projection of liquid drops. When the effervescence is at an end we heat gently to complete the action, and wash out the funnel with a little water, which is then received in the capsule. We add, whilst stirring up the liquid with a glass rod, 10 c.c. of concentrated sulphuric acid (2 c.c. per grm. of metal). There is produced a bulky pulp which re-dissolves on stirring and heating. We evaporate gently, either over a small rose-burner, stirring constantly for a quarter of an hour, or leaving it on the sand-bath for a longer time. The mass soon becomes pasty and then dry, becoming reduced to grains which are easily crushed with the stirring-rod.

It is placed on the stove and kept for two hours at a temperature of 120—125°, so as entirely to expel the nitric acid and render the silica throughout the mass quite insoluble. It is then re-dissolved in 50 c.c. of boiling water, and washed on a filter with an equal quantity of water, receiving the liquid in a litre flask.

The silica remains on the filter. It is generally coloured black or grey by graphite, and may be mixed with manganese peroxide. The latter is dissolved above another flask in a little concentrated hydrochloric acid and washed with hot water. We ignite to burn off the graphite and weigh the silica, which will have become white. This weight, multiplied by the coefficient 0·4667, gives an exact determination of the silicon, as in Drown and Shimer's method.

The filtrate contains the organic compounds derived from the transformation of the iron carbide under the action of the acids which might hinder the precipitation of the phosphoric acid. In order to burn the organic matter we add about 1 grm. of chromic acid and heat for half an hour to the temperature of ebullition. This operation has the advantage of certainly restoring to the state of orthophosphoric acid any trace of pyrophosphoric acid which may have been formed during the evaporation to dryness.

We then pour into the liquid 60—80 c.c. of a molybdic solution at 5 per cent prepared as usual, and keep it at 100° for two or three hours, the time necessary for a complete precipitation. It is allowed to settle and cool, and the liquid is decanted upon a filter and the deposit is washed in the flask with luke-warm water containing 1-20th of its volume of molybdic solution until the washing water is only coloured a very slight rose by the addition of ammonium sulphocyanide, *i.e.*, until they contain merely negligible traces of iron.

We then dissolve the precipitate in the flask with 30 c.c. of ammonia, diluted with an equal volume of hot water, and placing the funnel with the filter upon a small flask holding 150 c.c., into which the acid liquid has been decanted, we introduce the ammoniacal solution. We wash the flask and the filter with 50 c.c. of boiling water, slightly ammoniacal, making use of the filter-pump.

The filter may retain small quantities of ferric hydrate and phosphate, which are re-dissolved in a few drops of hot, dilute nitric acid, which are subsequently added to the acid liquid.

The ammoniacal solution, filtered and cooled, is gradually neutralised by nitric acid, not raising the temperature above 40°. When a yellow precipitate begins to appear, which does not re-dissolve on stirring, we add as a surplus 3 c.c. of pure nitric acid and the small quantity of dilute acid which has served to wash the filter.

It is left for two hours at a temperature of about 40° for the precipitation of the ammonium molybdate. The liquid is then decanted upon a tared filter and replaced by water acidified with 1 per cent of nitric acid. After two or three washings the precipitate is placed upon the filter, washed with a little distilled water by means of the pump, dried at 100° in the stove, and weighed in a small special bottle with a wide mouth so that the filter may be introduced without breaking.

By this second precipitation of ammonium phosphomolybdate in conditions of temperature and acidity perfectly defined, we obtain a product of constant composition free from iron and from excess of molybdic acid, which is not regularly effected with the first precipitation. The weight of the phosphorus present is obtained by multiplying the weight of the dried precipitate by the coefficient 0·01628.—*Comptes Rendus*, vol. cxvi., p. 105.

# ON CATHODIC RAYS IN GASES AT THE ATMOSPHERIC PRESSURE AND IN AN EXTREME VACUUM.*

By Dr. PHILIPP LENARD (of Bonn).

The rays exciting phosphorescence, proceeding from the cathode of a Geissler tube, permeate thin metal leaves, as Herr Hertz has shown. If it were practicable to find a metallic leaflet of such a thickness that with perceptible permeability it still closes air-tight and is capable of bearing the pressure of the atmosphere on one side only, it would be sufficient to close an opening in the side of a discharge tube with such a plate in order to allow those rays a passage into the open air. This thought has been realised in the experiments which will in the sequel be briefly described to the Academy. It is shown that the cathode rays when once produced propagate themselves into space filled with air. Thus their observation is greatly facilitated, and it is possible to select and to vary the conditions of observation independently of those of their origin.

## *The Apparatus.*

The figure shows a section of a convenient arrangement of the apparatus. E, E is the glass discharging tube, K the cathode, an aluminium disc of 12 m.m. in diameter, A the anode, which should preferably have a very large surface. Opposite to the cathode the tube is closed with a strong metal plate, M, M, which is perforated at F to the width of 1·7 m.m. Above this aperture there is cemented from without a hammered aluminium plate of 0·003 m.m. in

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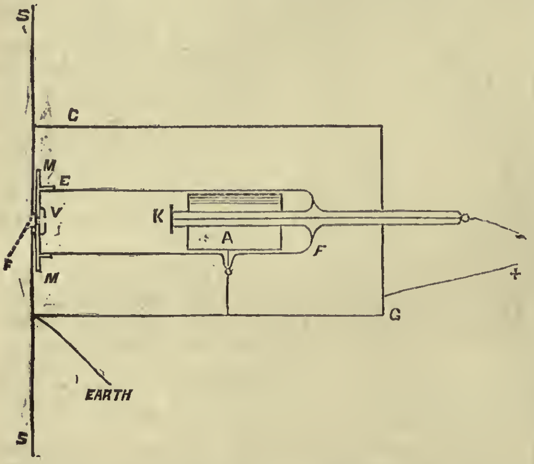
* A Paper read before the Royal Prussian Academy of Sciences at Berlin, in the Session of January 12, 1893.

thickness. We name this closing, which is permeable for cathode rays, but quite impermeable to air and light, the *window*, and the space to the left of it in the figure the space for observation. The distance of the cathode from the window is 12 centimetres; the latter is protected by the internal screen, V, from the extent of the discharge, and consequently from corrosion. Outwardly the large metal screen, S, S, is in conductive connection with the window side, to which the sheet-metal case, G, G, is again connected. The case, the screen, and the anode, as also the positive pole of a large inductorium, are connected to the earth, whilst its negative pole is connected with the cathode. The arrangement selected keeps the space for observation almost perfectly free from light and from the electric powers of the discharge.



The most favourable exhaustion in the discharging tube is reached when the potential difference between its electrodes corresponds to a striking distance of three centimetres between balls in air. As regards the phenomena which appear in the observation space, I have been able to establish the following, in addition to some less important points.

### *Cathode Rays in the Open Air.*

1. The cathode rays render the air faintly luminous. A halo of bluish light surrounds the window, and is moderately bright only on its surface. A strong odour of ozone is recognised.

2. Substances capable of phosphorescence, if held near the window, shine with their peculiar light on the side nearest the window. With an increasing distance from the window, the phenomenon rapidly decreases in intensity, and disappears at a distance of about six centimetres. Only the magnitude of the distance determines the brightness of the light; their direction is of no importance, which is not surprising, since cathode rays pass in a diffused manner through aluminium (H. Hertz, *Wied. Ann.*, vol. xlv., p. 31). Alkaline earthy phosphides, ordinary and uranium glass, calc-spar, fluor-spar, and other minerals, pentadecylparatolylketon, and asaron, all give out a light of the same colour and relative brightness as they do in exhausted spaces in the region of the cathode rays. The intensity is peculiarly strong with the alkaline earthy phosphides and the above-named carbon compounds. Among liquids, a drop of petroleum displayed its blue fluorescence. Metals, quartz, mica, and eosine gelatin (strongly excitable by light) remained non-luminous, as in exhausted tubes, as also aqueous solutions of eosine and fluoresceine, and the ethereal solution of chlorophyll.

All the phenomena of phosphorescence in the observation space cease if a magnet applied to the discharge tube repels the cathode rays from the inner surface of the window.

3. A quartz plate, one-half m.m. thick and not too small, inserted at any place between the window and the phosphorescible body, causes the extinction of the light. An ordinary foil of gold, copper, or aluminium permits it to remain scarcely weakened. Whether a substance proves permeable or not depends entirely on the thickness of the stratum employed. I have met with no solid body which is perceptibly permeable at the thickness of one-fifth m.m, or upwards, but thin layers of almost all substances were partially permeable. Thus stout writing-paper, collodion films, aluminium foil even rolled to the thickness of 0·03 m.m., glass blown thin, and mica split very thin. In addition to the metal foils above mentioned, silk, paper, and soap bubbles form screens almost absolutely permeable; they show colours below the sixth order.

4. The atmosphere is a dull medium for cathode rays; they do not spread out in it rectilineally, but in a diffused manner. The phosphorescent action penetrates deeply into the shadow of an opaque body supposed to be projected from the window, and it is not possible to separate by means of diaphragms sharp rays of a centimetre in length. If there is a metal plate with a sharply defined aperture about 1 m.m. in width in the way of the cathode rays —say at a distance of 20 m.m. from the window—and if we examine the space behind the plate with a phosphorescible screen, we find a sharp bright figure of the aperture only close behind it; even at a distance of 3 m.m. the image is magnified five-fold and indistinct, and at a distance of 12 m.m. the screen is everywhere almost uniformly illuminated.

### *Cathode Rays in a Vacuum.*

For the nature of the cathode rays it is a fundamental question whether their propagation depends on the presence of matter or if it takes place in void space. The impossibility of producing cathode rays in a complete vacuum has hitherto prevented the solution of this question. It is now possible to evade this hindrance; we produce the rays as heretofore, enclose the observation space with glass walls, and exhaust it.

The further the evacuation proceeds, the greater becomes the distances at which the phenomena of phosphorescence can be recognised, and the more distinctly the rays are simultaneously separated by a diaphragm. If that high degree of exhaustion is reached at which the cathode rays are generally studied, the phenomena of phosphorescence (which are now very bright) display on the glass side of the observation space a rectilinear extension in all directions from the window. The length of the rays, which are now almost sharp (30 c.m.), is only limited by the sides. From this exhaustion to the utmost possible there now occurs little more change. The rays seem to become still rather sharper, and the phosphorescence of the glass rather brighter. At this extreme exhaustion at which the mercurial air-pump ceases to act, even the most sensitive test for a gaseous residuum, the electric discharge, fails us. It is no longer possible to produce a discharge between the aluminium plates fused into the observation space. The interchange ensues externally along the glass side, although the distance of the electrodes is 20 c.m. To such imperceptible residues of matter we cannot ascribe any perceptible effects. If this is conceded, our experiment as to the nature of the cathode rays decides that they are processes in the ether. If they were processes in matter, that space would have been for them substantially impermeable. To the experiments in this section it must be remarked that at all degrees of exhaustion that admitted of a somewhat distinct formation of rays they are found to be strongly deflected by the magnet.

### *Cathode rays in Various Gases.*

6. Various gases are turbid media in very different degrees; greater permeability is connected with greater

clearness. If we allow coal-gas to issue between the window and a phosphorescible screen, we perceive considerable clearing on the screen. If we now again fill the observation space, enclosed between glass sides, with hydrogen at ordinary pressure, the phenomena of phosphorescence extend for 20 c.m. from the window, *i.e.*, more than three times as far as in atmospheric air at the same pressure. At the same time we may, by means of a diaphragm, separate rays which up to about the length of 3 c.m. give moderately sharp phosphorescent spots. These rays, in hydrogen at a moderate pressure, are strongly deflected by the magnet. Oxygen is perceptibly less permeable than air and about equally turbid. Carbonic acid is much less permeable; in this gas all the phenomena are confined to distances below 4 c.m. from the window; rays, even of the length of a few millimetres, cannot be obtained.

To conclude from this behaviour of gases in the processes which make up the essence of the cathode rays extremely minute dimensions must come into consideration. Even to light of the shortest known wave-lengths matter seems to fill space continuously. But here the behaviour, even of elementary gases, is that of a non-homogeneous medium, each single molecule appears as a distinct obstacle, The number of mols. upon which the cathode rays impinge in equal volumes of different gases is always the same; whence we may say that hydrogen molecules obscure the ether much less than the molecules of oxygen, and these, in turn, less than molecules of carbon dioxide.

## THE SIMULTANEOUS PRECIPITATION OF COPPER AND ANTIMONY BY THE GALVANIC CURRENT.

By W. HAMPE.

The author shows that all the commercial brands of electrolytic copper which have been examined in his laboratory along with from 99·94 to 99·99 per cent of copper always contained small quantities of antimony, in good sorts from 0·007 to about 0·02. This fact shows that in the technical elaboration by means of electrolysis small quantities of antimony are always precipitated along with the copper.

Also in the determination of copper, as practised in the laboratories by the electrolysis of its sulphuric solution acidified with free nitric acid, antimony, if present, falls not only, as heretofore supposed, *after* the precipitation of the copper, but to a small extent also simultaneously. This fact must be taken into account in separations and in quantitative determinations of copper in order to avoid errors. The less antimony is present in the solution as compared with the copper, and the earlier the electrolysis is broken off the less antimony is precipitated along with the copper. The tension and the density of the current are not without influence. The following observations indicate the quantities of antimony deposited along with the copper under defined conditions.

1. A copper sulphate containing 25·09 per cent of copper, 0·0083 per cent of antimony (corresponding to a copper with 0·033 per cent of antimony), gave on the electrolysis of its saturated solution acidified with 20 c.c. nitric acid, with six Meidinger-Pincus globe elements, a copper containing 0·007 per cent antimony.

2. 45·896 grms. of an alloy of copper and antimony were treated with nitric acid, whereon the antimony partly passed into solution and partly remained undissolved as antimonic acid. Without separating the latter from the liquid it was evaporated down along with an excess of concentrated sulphuric acid until dense vapours escaped, and the residue was taken up with water and 20 c.c. nitric acid. After the undissolved part of antimonic acid was filtered off it was submitted to electrolysis, the current being interrupted whilst the liquid was still distinctly coloured. It contained, as appeared on its further treatment with hydrogen sulphide, &c., still 0·3644 grm. copper along with antimony. The latter, along with the antimony of the undissolved residue, amounted to 0·2338 grm. The metallic deposit thus obtained electrolytically was of the finest rose colour, like chemically pure copper. Its weight was 45·284 grms. It was dissolved off the core by means of nitric acid, the solution was evaporated down with an excess of sulphuric acid until all nitric acid was expelled, the residue was taken up with water, and from the strongly acid solution the copper was thrown down by means of potassium sulphocyanide and sulphurous acid as a sulphocyanide.

The filtrate was worked up by well known methods, and was found to contain 0·009 grm. antimony which had been precipitated along with 45·275 grms. copper, so that the metallic precipitate had contained 0·0198 per cent antimony. From the above data the composition of the original alloy is computed as 99·441 per cent copper and 0·529 per cent of antimong. It also contained 0·015 per cent of iron.

It must be mentioned that the acids employed, prior to their use, had been freed from any antimony present. They had been diluted, treated with hydrogen sulphide, decanted, and again concentrated by evaporation.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, February 13th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 163 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In respect to its general characters, and especially to the smallness of the proportion of organic matter present, the condition of the water supplied to the Metropolis during the month of January was, notwithstanding the unfavourableness of the season, entirely satisfactory. Thus, taking the Thames-derived water for comparison, the mean amount of oxygen required for oxidation was found to be 0·052 grain per gallon, as against a mean of 0·068 grain per gallon for the previous two months' supply. Again, the mean proportion of organic carbon was found to be 0·159 part in 100,000 parts of the water, with a maximum of 0·248 part in any single sample examined, as against a mean of 0·198 part and a maximum of 0·286 part in the previous two months' supply.

The condition of the water was, however, not uniform throughout the month. With the prolongation of the frost—prevailing more or less continuously through the last week of December and first three weeks of January —and more particularly on the breaking up of the frost at the end of the third week of January, there was a noticeable, though indeed wholly unimportant, increase in the proportion of organic matter present both in the Thames-derived and in the Lea-derived water, as estimated alike by the "combustion" and "oxidation" processes. The increase, however, in the degree of colour tint of the water—usually, but not always proportionate roughly to the amount of organic matter present—was more decided, and in several of the samples of Thames water examined during the latter half of the month, reached and even exceeded the limit of the scale.

Despite the difficulties incident to the conduct of the process of filtration in time of frost, the whole of the 163 samples examined were found to be well filtered, clear, and bright.

We are, Sir,
Your obedient Servants,

William Crookes.
William Odling.

## ON STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

In Russia many works make at present very good steel castings. Principally open-hearth steel is used, though several works employ crucible steel. The Obouchoff Steel Works, near St. Petersburg, use crucible steel, preparing it in coke furnaces (four crucibles to each furnace). They have and always had extensive orders from the navy for gun-carriages. When we were connected with these works, the steel for casting the different parts of gun-carriages was prepared as follows:—Each crucible was loaded with forty pounds of puddled iron (0·12 per cent of carbon), and forty pounds of puddled steel of medium hardness (0·45 to 0·50 per cent of carbon). Finally, to this charge one-half to three-quarters of a pound of ferromanganese, containing 70 per cent of manganese, was added.

The crucibles are placed into the furnaces, and in about four and a half hours the charge is melted. Next to each crucible by means of an iron funnel is added two and a half pounds of silicon iron, containing 7 per cent of silicon. After a lapse of twenty minutes the casting of steel is commenced. The moulding sand is prepared from 85 per cent of white quartz sand, used for the formation of the open-hearth furnace lining at the same works, which is mixed with 15 per cent of good fire-clay and a small quantity of rye-flour, in order to render the moulds porous after heating them in the drying-stove.

The Poutiloff Iron and Steel Works, near St. Petersburg, use for small castings up to 10 poods crucible steel, and for heavy castings open-hearth steel is used. They frequently receive orders from the navy for rudder-frames, stem-posts, stern-posts, shaft brackets, &c.

For instance, the Poutiloff Works lately executed the castings of a stem and stern posts for a gun-boat. Open hearth steel was used, and the addition before the casting consisted of ferrosilicon. The following are the chemical analyses:—

| | Stem. | Stern. |
|---|---|---|
| | Per cent. | |
| Carbon.. .. .. .. .. | 0·13 | 0·15 |
| Manganese .. .. .. | 0·50 | 0·45 |
| Silicon .. .. .. .. .. | 0·27 | 0·25 |
| Phosphorus.. .. .. | 0·03 | 0·04 |
| Sulphur . .. .. .. .. | 0·02 | 0·02 |

The mechanical tests gave the following results:—Stem-post, breaking strain 32·5 tons per square inch, elongation in eight inches 12·3 per cent; stern-post, breaking strain 34·8 tons per square inch, elongation in eight inches 11·2 per cent. The Government commission found these tests satisfactory and adopted the castings. We prefer the use of ferrosilicon, or still better, silicospiegel (10 per cent of silicon and 12 per cent of manganese). Sound and good steel castings are always obtained. After casting, the products must contain 0·25 to 0·30 per cent of silicon.

In general, when making steel castings we ought to remember that even in the last century Reaumur defined steel as a compound of iron and carbon, so that we must suffer the introduction of a small quantity of silicon only as an inevitable evil and then only as a necessity, in order to obtain a sound steel without forging the metal.

### ON THE
## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 92).

In our calculation of the presumable effect of the sulphurous acid on the result of Dumas's syntheses, we neglected the error caused by the sulphurous acid contained in the surplus hydrogen which goes out of the water-receptacle through the action of the vitriol contained in the drying tubes included in the latter. As the quantitative effect of *this* sulphurous acid is difficult to predict, we tried to determine it by direct experiments. But, in doing so, we had our eyes more on our own "First Series of Syntheses" (*vide infra*) than on Dumas'; we therefore used small U-tubes charged with vitrioled pumice, such as we had used in our own syntheses. A current of hydrogen, purified by means of a tower of caustic soda and red-hot copper gauze, was passed through (1) a tube containing phosphoric anhydride; (2) a similar tube charged with the same reagent; (3, 4, and 5) three successive U-tubes charged with vitrioled pumice; and from the last vitriol tube the gas passed into the graduated Pisani.

*Experiment* I.—Volume of hydrogen used = 3·5 litres. Temperature = 17·5—17·8° C. The second $P_2O_5$-tube gained 0·1 m.grm., the three vitriol tubes

| | (3) | (4) | (5) |
|---|---|---|---|
| Lost.. .. .. .. .. | 0·3 | 1·6 | 4·8 m.grms. |

*Experiment* II.—Volume of hydrogen used = 6 litres. Temperature = 16·5—17° C. The second $P_2O_5$-tube gained 2·3 m.grms., the three vitriol tubes

| | (3) | (4) | (5) |
|---|---|---|---|
| Lost.. .. .. .. .. | 0·3 | 1·0 | 0·0 m.grm. |

*Experiment* III.—In this experiment a tube charged with recently-fused caustic potash was substituted for the first phosphoric acid tube. Volume of hydrogen used = 9·5 litres. Temperature not observed. The $P_2O_5$-tube gained 0·3 m.grm., the vitriol tubes

| | (3) | (4) | (5) |
|---|---|---|---|
| Lost.. .. .. .. .. | 1·2 | 1·9 | −0·1 m.grm. |

The tubes (3) and (4) correspond to the two vitriol tubes which were attached to our water-receptacle, and weighed before and after the synthesis. The conjoint loss of these two tubes in

| Experiments .. .. | I. | II. | III. |
|---|---|---|---|
| was .. .. .. .. .. | 1·9 | 1·3 | 3·1 m.grms. |

The error, as we see, is not very considerable, but it is too great to be neglected, and with Dumas's very large U-tubes, it must have been greater than in our case. That the witness tube in Experiment I. lost almost 5 m.grms. is an anomaly which we cannot explain.

Of the several sources of error in Dumas's experiments,

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* *Proceedings of the Philosophical Society of Glasgow.*

which we are able to see, only one remains to be considered. We allude to the unavoidable presence of *occluded hydrogen* in the metallic copper produced. Dumas was quite alive to this source of error, and, indeed, caused Melsens to determine its magnitude. In one of Melsen's experiments the metallic copper produced from 300 grms. of oxide by reduction hydrogen, when re-burned in oxygen, gave 65 m.grms. of water = 7·2 m.grms. of hydrogen or 0·000119 grm. per grm. of oxygen in the oxide of copper started with. Dumas states that once, when the reduction of the oxide was effected at an exceptionally low temperature, the copper contained 0·0002 of its weight of hydrogen. In this case the weight of hydrogen per grm. of oxygen in the original oxide was 0·0008 grm.

In the course of our first series of syntheses we sometimes determined the occluded hydrogen in the metal produced, and we may as well communicate the results now. After the completion of a synthesis of an evening, the reduction-tube was stopped up and kept over night. On the following morning the tube was re-weighed, to make sure that it had not changed weight, or to determine any change that might have taken place. It was then heated in a current of air, dried by means of vitrioled pumice, until it had suffered a very far-going oxidation, the water being collected in a tared U-tube charged with vitrioled pumice and weighed. In the following table the headings refer to the pages of our journal.

| | Page— | | | |
|---|---|---|---|---|
| | 44. | 45. | 67. | 71. |
| Oxygen used as oxide of copper, grms. .. .. | 2·876 | 4·805 | 4·262 | 5·539 |
| Water formed, in m.grms. .. .. .. | 0·3 | 0·1 | 2·4 | 2·9 |
| Occluded hydrogen .. | 0·03 | 0·01 | 0·27 | 0·32 |
| Hydrogen, per grm. of oxygen, m.grms. .. | 0·1 | 0·002 | 0·0626 | 0·0582 |

| | Page— | | | |
|---|---|---|---|---|
| | 75. | 77. | 79. | 89. |
| Oxygen used .. .. | 10·372 | 10·526 | 10·424 | 15·460 |
| Water produced .. .. | 3·7 | 2·7 | 2·1 | 7·2 |
| Occluded hydrogen .. | 0·41 | 0·3 | 0·23 | 0·8 |
| Ditto, per grm. of oxygen, m.grm. .. | 0·0396 | 0·0284 | 0·0224 | 0·0518 |

Taking $\delta$ as a symbol for the occluded hydrogen per grm. of oxygen used apparently as oxide of copper, if the water obtained in the synthesis per 1 grm. of loss of weight suffered by the oxide of copper was $=k$, the true value $k_0$ of the ratio $H_2O : O$ is $k\ (1-\delta)$. Now, our highest value for $k\ \delta$ was 0·000071 grm., hence $k-k_0=$ 0·000071. Supposing, for instance, the true $k_0$ were equal to 1·125, then $k=$1·125071, corresponding for O = 16, to H = 1·000568.

But our average value for $\delta$ is only 0·0000344, hence $k-k_0=$0·000039, corresponding to H = 1·000312. From Melsens's experiment with the metal from 300 grms. of oxide we should have H = 1·00100. Our conclusion at the time was that the influence of the occluded hydrogen may safely be neglected.

To sum up:—Assuming Dumas's hydrogen contained the proportion of atmospheric oxygen corresponding to our determination V. (see p. 71), and 0·91 m.grm. of $SO_2$ per litre (see p. 91), then his (uncorrected) value $k=$1·12547 for $H_2O : O$ is liable to the following corrections:—

1. On account of the oxygen.. .. .. .. −0·000287
2. On account of the sulphurous acid .. −0·00154

Total .. .. .. .. −0·001827

Hence, corrected value $k=$1·12364. All this on the assumption that the water-weights of Dumas are the *true weights*. If he forgot to reduce these to the vacuum, the corrected $k$ must be corrected up by 0·001227 × 1·12547 = 0·00138, so that we have, for the fullly corrected $k'$ the number 1·12502; whence, for O = 16, H = 1·00016!

Let us now pass to a consideration of Erdmann and Marchand's work.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, February 2nd, 1893.*

Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

Mr. Walter H. Ince was formally admitted a Fellow of the Society.

Ordinary certificates were read for the first time in favour of Messrs. John Frederick Briggs, c/o Messrs. Parry and Co., Madras; Julian L. Baker, Stamford, Hendham Road, Upper Tooting, S.W.; William A. Bone, Schlossberg, 3, Heidelberg; H. W. Dickinson, Kent Place, Ulverston, Lancashire; John Addyman Gardner, 5, Bath Place, Oxford; John Alan Murray, 60, Marine Terrace, Aberystwyth; Alan E. Munby, 44, Holly Avenue, Newcastle-on-Tyne; J. Frank McGregory, M.A., Hamilton, N.Y., U.S.A.; James Henry Robbins, 4, Roderick Road, Haverstock Hill, N.W.; William Rintoul, 48, Carnarvon Street, Glasgow; George Rudd Thompson, 5, Clytha Square, Newport, Mon.

Of the following papers, those marked * were read:—

*106. "*The Connection between the Atomic Weight of the Contained Metals and the Magnitude of the Angles of Crystals of Isomorphous Series.*" By Alfred E. Tutton, Assoc. R.C.S.

The author has subjected the crystals of twenty-two salts of the series of double sulphates $R_2M(SO_4)_2{\cdot}6H_2O$ containing as the alkali metal R potassium, rubidium, and cæsium respectively, and as the second (dyad) metal M magnesium, zinc, iron, manganese, nickel, cobalt, copper, and cadmium respectively, to a detailed goniometrical investigation, with the purpose of ascertaining the nature of the connection specified in this title. The measurements have been made in great detail, at least 10 crystals of each salt, of the highest procurable degree of purity and perfection, selected from several different crops, having been completely measured: an average of over 400 measurements have thus been made in the case of each salt, 40 separate values of each of the principal angles being frequently obtained; this being considered necessary in view of the smallness of the differences under investigation, in order that on taking the mean of all the values of each angle the errors due to slight disturbances during deposition, and also the instrumental errors, might be eliminated. The purity of each salt was established by direct analysis. The twenty-two salts are fully described in the paper, and complete tables of their angles given. After each set of three salts containing the same second metal and potassium, rubidium, and cæsium, respectively, as the alkali metal have been thus described, their angles are compared and the morphological relations are discussed.

The results of the investigation are embodied in the following summary:—

1. The salts containing cæsium as the alkali metal are the most readily obtained in the form of crystals; those containing potassium the least; the salts containing rubidium occupying an intermediate position in this respect.

2. Though bounded by the same common planes, the crystals of the potassium, rubidium, and cæsium salts of the series exhibit specific characteristic habits, the characteristic habit of the crystals of the potassium salts being widely different from that exhibited by the crystals

of the cæsium salts, and the habit usually assumed by the crystals of the rubidium salts being of an intermediate character. The relations between the characteristic habits of the potassium, rubidium, and cæsium salts respectively are thus found to be in direct correlation with the atomic weights of the alkali metals.

3. The axial angle $\beta$ increases with the increase in the atomic weight of the alkali metal, its magnitude in any rubidium salt of the series being approximately midway between that in the potassium and that in the cæsium salt containing the same second metal; in other words, the differences between the magnitudes of the axial angle in crystals of this series containing potassium, rubidium, and cæsium respectively as the alkali metal are in direct simple proportion to the differences between the atomic weights of these metals.

The changes in the magnitude of the axial angle on passing from a potassium to a rubidium salt, and from a rubidium to a cæsium salt, are very considerable, usually exceeding a whole degree in each case; they are therefore far outside the limits of possible experimental or formational error.

4. The magnitudes of all the angles between the faces of the crystals of the salts of this series containing rubidium as the alkali metal lie between the magnitudes of the corresponding angles upon the crystals of the salts containing potassium and cæsium respectively.

The differences between the magnitudes of the angles other than the axial angle, in crystals of this series containing potassium, rubidium, and cæsium respectively as the alkali metal are not generally in direct simple proportion to the differences between the atomic weights of these metals. The maximum deviation from simple proportionality occurs in the prism zone, in which the ratio of the difference varies, according to the nature of the second metal present, from 1 : 2 to 1 : 3.

The fact that the differences between the magnitudes of many of the angles of the cæsium and rubidium salts are so much larger than those between the rubidium and potassium salts would appear to indicate that as the atomic weight increases, it exercises an influence on these angles in excess of the mere numerical proportion to its increase. This influence is most apparent in the case of the angles of the prism zone, and becomes less and less evident in the zones approaching more and more nearly to the plane of symmetry, until at length, in the case of the axial angle lying in the plane of symmetry, all evidence of it disappears, and the differences are then directly proportional to the numerical differences in atomic weight.

5. The alkali metals exert a preponderating influence in determining the geometrical form of the crystals, the magnitudes of the angles being altered on displacing one alkali metal R by the next higher or lower to an extent attaining a maximum in certain angles of more than a whole degree, while the displacement of the second (dyad) metal M by any other of the same group is unattended by any material change in the angular magnitudes.

6. The importance of the axial ratios as indicative of the change of geometrical form on displacing one alkali metal in any salt of the series by another is greatly diminished by the fact that simultaneous changes more or less neutralising each other occur in the angles which determine them, thus causing the differences to be small. It is generally observed, however, that in any set of three salts containing the same second metal the ratios in the case of the rubidium salt lie between those of the potassium and cæsium salts, and somewhat nearer to those of the potassium salt. The changes in the angles themselves afford the only complete information concerning the change in geometrical form.

The optical properties of the crystals of the salts now considered will be described and discussed in a subsequent communication.

### Discussion.

Mr. Miers remarked that Mr. Tutton appeared to attribute the intermediate position occupied by the rubidium sulphates to the fact that the atomic weight of rubidium is the arithmetic mean of those of potassium and cæsium; if this were the simple cause, we should expect similar relations to obtain in the lithium, sodium, and potassium, or the calcium, strontium, and barium series, or in the case of an homologous series of hydrocarbon radicles. The strontium salts, however, are not intermediate in form between those of barium and calcium in the case of the bromates, the sulphates, or the carbonates, and even in the potassium-rubidium-cæsium series the platinonitrites and the platiniodonitrites prepared by Nilson afford results showing that the rubidium salt does not necessarily occupy an intermediate position. Hence it is impossible at present to draw simple general conclusions from the results afforded by these or other isomorphous series, as the relations obtaining in one series do not generally prevail in others. Mr. Miers expressed the hope that Mr. Tutton would extend his observations to the isomorphous selenates.

*107. "*The Preparation of Phosphoric Oxide free from the Lower Oxide.*" By W. A. Shenstone and C. R. Beck.

A description is given of a method of preparing phosphoric oxide free from the lower oxides by distilling it over platinum sponge in the presence of excess of oxygen. The authors refer to a similar process lately described by Professor Threlfall (*Phil. Mag.*, January, 1893), and call attention to certain points in this process which in their experience considerably improve its efficiency and value.

### Discussion.

Professor Thorpe, referring to the strictures passed on the commercial phosphoric oxide by Mr. Shenstone, said that in his experience it was by no means unsatisfactory in quality. Mr. Tutton and he had failed in extracting more than a minute proportion of phosphorous oxide from it.

Mr. H. B. Baker agreed with Professor Thorpe; he had been in the habit of testing for the tetroxide by means of carbon tetrachloride, which dissolves it but not phosphoric oxide.

Mr. Shenstone, in reply, said he had not intended to imply more than that the commercial product was impure; the percentage of impurity was probably small.

*108. "*Contributions to our Knowledge of the Aconite Alkaloids.* Part IV. *On Isaconitine (Napelline).*" By Wyndham R. Dunstan and E. F. Harrison.

The authors have investigated the nature and properties of the alkaloid found together with aconitine in the roots of *Aconitum napellus* (see Part II.), to which it was proposed to assign the old disused name of napelline; this alkaloid always occurs in the roots to as large an extent as aconitine and in some cases to a larger extent. The preparation of the pure substance is fully described in the paper. Its separation from aconitine is based on the superior solubility of the latter in ether, while its superior solubility in chloroform affords a means of separating it in greater part from the other associated alkaloids; it is finally purified by re-crystallising its hydrochloride. It is found to be *isomeric* with aconitine, and the name *isaconitine* is therefore now adopted instead of napelline, to which objections were raised on a former occasion.

Isaconitine has hitherto always been obtained in a colourless friable varnish-like form, resisting all attempts to crystallise it; it is readily dissolved by alcohol and chloroform, less readily by ether, and it is only slightly soluble in water, though more so than aconitine. The alcoholic solution is feebly dextro-rotatory.

The *hydrochloride*, $C_{33}H_{45}NO_{12}\cdot HCl$, crystallises from water in rosettes soluble in alcohol, containing 1 mol. prop. of water. The aqueous solution is intensely bitter, and is lævo-rotatory to almost the same extent as the aconitine salt, $[\alpha]_D = -28{\cdot}74°$.

The corresponding *hydrobromide* and *hydriodide* form similar crystals, but are anhydrous; the latter salt is lævorotatory, $[\alpha]_D = -26{\cdot}94^\circ$. All these compounds somewhat resemble the corresponding aconitine salts in their physical properties.

Isaconitine exhibits a remarkable behaviour with auric chloride which sharply distinguishes it from aconitine, and, indeed, from most other alkaloids. Hitherto no definite *aurichloride* has been obtained, but it is found that when solutions of the hydrochloride and of auric chloride are mixed, a yellow amorphous precipitate is produced as in the case of aconitine; on re-crystallising this from alcohol, nearly colourless crystals are obtained of an *aurochlorisaconitine*, of the formula—

$$C_{33}H_{44}(AuCl_2)NO_{12}.$$

This is apparently a derivative of the alkaloid in which one atom of hydrogen is displaced by the group $AuCl_2$. The first known alkaloidal derivative of this type, namely, aurochlorcaffeine, was described a short time ago by Dunstan and Shepheard (*cf. Trans.*, Feb., 1893). The production of such a compound from napelline was altogether unexpected. Aurochlorisaconitine differs, however, from aurochlorcaffeine in not being re-converted into the aurochloride by the action of hydrogen chloride.

When isaconitine is heated either with water in closed tubes or under ordinary pressure with mineral acids, it is gradually hydrolysed. The hydrolysis is more rapidly effected by aqueous solutions of soda or potash, which act even in the cold. It yields the same products as aconitine and the same proportions, viz., aconine and benzoic acid, $C_{33}H_{45}NO_{12}+H_2O=C_{26}H_{41}NO_{11}+C_7H_6O_2$.

The physiological action of isaconitine has been compared with that of aconitine by Professor Cash, who finds that the action of the two alkaloids is entirely distinct. A solution of a pure isaconitine salt does not produce the tingling sensation on the tongue which is so characteristic of aconitine; and while aconitine is a most violent poison, even in excessively minute doses, relatively considerable quantities of isaconitine must be administered to small animals in order to produce a toxic effect, which effect is the result of a physiological action in the main distinct from that of aconitine. It seems doubtful whether isaconitine would prove toxic to man, except when given in very large doses.

It may be added that the new alkaloid now described under the name of isaconitine is entirely different from the mixtures of amorphous alkaloids called napelline by the earlier workers. It also differs in composition and properties from the picraconitine of Wright, and the amorphous bases since obtained from the roots of *Aconitum napellus* by other investigators. Having regard to the manner in which these amorphous bases were prepared, and to the extreme difficulty which is experienced in preparing pure isaconitine, it may be safely concluded that they were not single substances.

*109. "*Contributions to our Knowledge of the Aconite Alkaloids.* Part V. *The Composition of some Commercial Specimens of Aconitine.*" By WYNDHAM R. DUNSTAN and FRANCIS H. CARR.

The authors have examined a number of English and foreign specimens of aconitine. For several of these they are indebted to Dr. J. W. L. Thudichum, who collected them some years ago; others have been purchased during the last two years. Dr. Thudichum had found that the various specimens differed enormously in their toxic power, many being nearly inert, while a few were highly poisonous.

The process used in examining these "aconitines" was essentially that described in the preceding communication, by means of which aconitine, isaconitine, homisaconitine (homonapelline), and aconine could be isolated, and the quantity of each approximately determined. The method of estimating aconitine first proposed by Wright, and recently advocated in a slightly modified form by Allen, in which the benzoic acid produced on hydrolysis of the mixture of alkaloids is reckoned as derived from aconitine, is valueless, since isaconitine furnishes benzoic acid in the same proportion as aconitine when hydrolysed. Sixteen specimens of "aconitine from *A. napellus*" and its salts were examined. Most of the samples were amorphous; these were invariably found to contain but a very small proportion of aconitine, in some cases none, but were chiefly composed of the amorphous alkaloids aconine, isaconitine, and homisaconitine, all of which appear to be very slightly, if at all, toxic. It would seem that, as a rule, "amorphous aconitine" represents the total alkaloids of the root. Of the crystalline specimens of alkaloid only two were pure, most of them being contaminated with more or less amorphous alkaloid. The specimens of aconitine salts examined were found, in nearly every case, to be chiefly isaconitine salts containing only small quantities of aconitine compounds. Hence it is not surprising that great differences have been observed in the mode of action and toxic power of commercial "aconitine." It is most important that in future nothing but pure crystalline aconitine possessing the characters fully described in Part I. of the enquiry should be used in medicine, and it is satisfactory that a pure alkaloid can now be obtained in commerce.

### DISCUSSION.

Mr. HOWARD characterised the discovery of the extraordinary difference between aconitine and the isaconitine now described as a striking example of the value of high "theoretical" chemistry; the discovery of the explanation of the difference would be of the deepest interest.

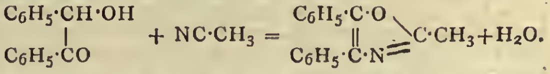
Dr. STEVENSON, after alluding to the impure nature of German commercial aconitine, dwelt on the importance of using crystallised material, which gave fairly constant results; such was the virulence of the alkaloid that 2/1,000ths of a grain never failed to kill a large mouse, and 3 m.grms. usually proved fatal to an adult man.

Dr. BRUNTON spoke of the fear of prescribing "aconitine" which existed owing to its irregular character; in the course of experiments made twenty-two years ago, he had himself obtained most conflicting results, having, doubtless, used different "aconitines." He then remarked on the scientific interest attaching to the determination of the nature of the alkaloidal constituents of the various species of aconite, and the light which might thereby be shed on the origin of the different alkaloids: *A. heterophyllum*, unlike most species, contained no poisonous principle, and it would be specially interesting to examine this.

Professor DUNSTAN, in reply, said that German aconitines were not all amorphous and valueless; moreover, it was a mistake to suppose that a sample was pure because it was crystalline. *A. heterophyllum*, to which Dr. Brunton had alluded, had a very bitter taste; as this was characteristic of isaconitine, perhaps this alkaloid was present.

110. "*Synthesis of Oxazoles from Benzoin and Nitriles.*" By FRANCIS R. JAPP, F.R.S., and T. S. MURRAY, D.Sc.

The authors find that nitriles and benzoin interact when a mixture of the two compounds is dissolved in concentrated sulphuric acid, water being eliminated, an oxazole being formed in which the hydrocarbon radicle attached to the cyanogen of the nitrile occupies the *meso*-position, *e.g.*, in the case of acetonitrile, which yields *αβ*-diphenyl-*μ*-methyloxazole (m. p. 28°),—



$$\begin{array}{l} C_6H_5{\cdot}CH{\cdot}OH \\ \quad | \\ C_6H_5{\cdot}CO \end{array} + NC{\cdot}CH_3 = \begin{array}{l} C_6H_5{\cdot}C{\cdot}O \diagdown \\ \quad \| \qquad\qquad C{\cdot}CH_3 \\ C_6H_5{\cdot}C{\cdot}N = \end{array} + H_2O.$$

In addition to the foregoing, they have prepared *αβ-diphenyloxazole*, $C_{15}H_{11}NO$ (m. p. 44°), from benzoin and hydrogen cyanide; *αβ-diphenyl-μ-ethyloxazole*, $C_{17}H_{15}NO$ (m. p. 32°), from benzoin and propionitrile; and *triphenyloxazole*, $C_{21}H_{15}NO$ (m. p. 115°), from benzoin and benzonitrile. Triphenyloxazole is identical with Laurent's *benzilam* and Zinin's *azobenzil.*

By heating $\alpha\beta$-diphenyl-$\mu$-methyloxazole with ammonia, it is converted into the corresponding imidazole, identical with Japp and Wynne's methyldiphenylglyoxaline, the oxygen atom in the ring being displaced by NH.

111. "*The Action of Nitrosyl Chloride and of Nitric Peroxide on some Members of the Olefine Series.*" By William A. Tilden and J. J. Sudborough.

The authors have examined the action of nitrosyl chloride on the first five members of the olefine series with the following results:— Ethylene forms only the dichloride; propylene and butylene a mixture of dichloride and nitrosochloride, while trimethylene (amylene) is almost entirely converted into a nitrosochloride. Phenylethylene (cinnamene) behaves like trimethylethylene. Further, it is now found that propylene affords a compound similar to that prepared by Guthrie many years ago from nitric peroxide and amylene. The study of these compounds has been undertaken with the view of elucidating the constitution of the nitrosochlorides formed by the terpenes.

112. "*Piperazine.*" By W. Majert and A. Schmidt.

Erroneous statements have appeared in several modern text-books regarding the physical and chemical characters of piperazine, $C_4H_{10}N_2$, which have been confused with those ascribed by A. W. von Hofmann and by Ladenburg to the impure substances of like composition discovered by them, and termed respectively diethylenediamine and ethyleneimine or diethylenediimine; our attention has been directed to the fact that this misunderstanding has partly arisen from a misconstruction of our views (*Ber.*, 1890, 3719) as to the identity of these substances: we, therefore, desire to correct this impression.

Piperazine, which was not known in its pure crystalline condition until prepared by us in August, 1890, by treatment of dinitrosodiphenylpiperazine with alkali, is a crystalline substance melting at 104—107° in capillary tubes, although when the melting point is determined on large quantities it is found to be 112°, the differences being due to the hygroscopic nature of the base; it boils at 140—145°. It is very readily soluble in water and alcohol, the aqueous solution having a distinctly alkaline action. It is very hygroscopic and readily absorbs carbon dioxide, being thereby converted into the carbonate melting at 162—165°.

Piperazine is especially characterised by the formation of an insoluble pomegranate-red double salt with bismuth iodide and by a dibenzoyl compound melting at 191°.

The basic substance diethylenediamine prepared by Hofmann by the interaction of ammonia and ethylene bromide consisted of a liquid mixture of bases boiling approximately at 170°. That this mixture contained a small quantity of a base identical with piperazine is undoubted, but it was only after piperazine had been prepared from dinitrosodiphenylpiperazine that Hofmann succeeded in identifying it and isolating the pure crystalline product from the mixture, which, besides higher ethylene bases, contained also a number of vinyl compounds.

Owing to the difficulty of purifying small quantities of the base, Ladenburg's experiments with diethylenediimine, obtained by the decomposition by heat of ethylenediamine hydrochloride, were unsuccessful: the product described by Ladenburg as the base was undoubtedly impure piperazine carbonate, as proved by its melting point, 159—163°.

In conclusion, it may be interesting to mention that we have succeeded in preparing the following series of hydrates of piperazine, that most readily formed being a hexhydrate which crystallises from dilute aqueous solutions:—

$C_4H_{10}N_2 \cdot H_2O$, m. p. 75°,
,, $2H_2O$, ,, 56°,
,, $3H_2O$, ,, 39—40°,
,, $4H_2O$, ,, 42—43°,
,, $5H_2O$, ,, 45°,
,, $6H_2O$, ,, 48°,

## NOTICES OF BOOKS.

*An Introductory Manual for Sugar-Growers.* By Francis Watts, F.C.S., F.I.C., Associate Mason College, Birmingham, and Government Chemist, Antigua. London and New York: Longmans, Green, and Co., 1893. Crown 8vo., pp. 151.

This work is an able attempt at the correction of one of our national sins of neglect. Any other Empire including such an extent of tropical and semi-tropical territories as does that of Her Majesty would long ago have made the cultivation of crops suitable for such climates the subject of the most careful and persistent experiment and study, and have distributed the information so gained among the colonists or those likely to become such. We, until lately at least, have been content to turn swine, sheep, oxen, and, *proh pudor*, goats, into the most fruitful lands. When foreigners have devised some product to compete with tropical crops, we have let judgment go against us, so to say, by default. Of this neglect a striking instance occurs in the very product discussed in the work before us. Beet-sugar, it is well known, was one of the weapons forged against us by perhaps the most astute and powerful of our enemies, and even yet it is diligently wielded against us.

We are, therefore, exceedingly glad to find Mr. Watts coming forward to instruct our planters in the scientific principles of agriculture as applicable in tropical climates. It is sad to see farmers skilled in all the mechanical routine of husbandry going out to the Colonies and either working in a quite unsuitable manner or seeking to grow crops which require cold and damp air and soils.

Mr. Watts expounds the rudiments of agricultural chemistry and vegetable physiology in a plain, intelligible manner. Thus, in the first chapter we have an account of plant cells, tissues, and fibro-vascular bundles, of the structure and function of roots, stems, and leaves. The second chapter introduces us to the components of soils, to the conditions affecting fertility, to nitrification, the action of leguminous crops in the fixation of nitrogen. Chapter III. deals specially with the sugar-cane, whilst Chapter IV. discusses manures. Here green-dressing—the ploughing in of certain green crops—is recommended as a source of nitrogen and as improving the condition of the soil, but the inability of farmyard manure alone to maintain fertility is fully admitted. Manures for the West Indies should always be of a concentrated character to economise freight. Basic slag is recommended as deserving more attention than it has hitherto received. The use of ferrous sulphate seems to have given favourable results in some experiments instituted by the author.

The fifth, sixth, and seventh chapters treat of the manufacture of sugar in its different stages. The relative advantages and disadvantages of diffusion as compared with crushing are discussed, the author considering that the success of the former process in the West Indies is problematical.

The eighth chapter speaks of hydrometers and their use. We regret to find that the planters still cling to Beaumé's instrument, which not only does not admit of ready re-calculation into direct specific gravity and weight per gallon, but exists in two, if not three, discrepant forms. If they would use Twaddell's hydrometer they could not fail to become convinced of its superiority.

The ninth chapter deals with the utilisation of molasses. Various processes applicable to beet molasses are useless for the product of the cane. The author does not bring into sufficient prominence the fact that beet molasses is unfit for human consumption. But as a general rule he recommends distillation, *i.e.*, the production of rum. This outlet has, however, been lessened by the circumstance that rum is now largely adulterated with grain-spirits and even with potato-whiskey.

We think that in this excellent work some reference might have been advantageously made to the practical researches of Prof. R. Galloway. The only error we can discover is that the atomic weight of platinum is still given as higher than that of gold. As a whole, Mr. Watts's treatise deserves warm approval and extensive study.

*Physics: Advanced Course.* By George F. Barker, Professor of Physics in the University of Pennsylvania. London: Macmillan and Co., 1892.

Any man who had studied physics a quarter of a century ago and had not kept up the subject, would find himself no little perplexed on opening this volume. It is not so much that he will encounter novel facts and new generalisations—though in the meantime important discoveries have certainly been made—as that admitted truths are viewed in a new light. The author defines physics as the science of energy, whilst chemistry he thinks may be regarded as the science of matter.

To this second definition exception may fairly be taken. Were there only one kind of matter within our reach, where would be our chemistry? At the same time this one kind of matter would have certain properties,—commonly known as its mechanical properties,—which might be a legitimate object of study.

After introductory considerations the author divides his subject into mass physics, molecular physics, and physics of the ether. The phenomena of sound are discussed in the first section as "energy of mass-vibration."

The laws of heat fall under the head of molecular physics, along with its transference, its sources, and thermo-chemistry. It is doubtful whether any of the theories of the origin of solar energy can be accepted in face of the results to which they lead. The view of the late Sir W. Siemens, as to the recuperation of the sun's heat, is not discussed.

The fourth part takes up the physics of the ether, commencing with the energy of ether vibration or radiant energy, commonly known as light. The characteristics of the ether are given with the necessary proviso that it is known only by its properties. The interesting fact is mentioned that while only 2·4 per cent of luminous waves are present in the radiation from a gas-burner, 10 per cent in that of an arc-light, and only 35 per cent in that of the sun, the radiations of the fire-fly (*Pyrophorus noctilus*) are wholly composed of visible wave-lengths. Here, therefore, is a field for the inventor!

It is shown by the researches of Prof. Langley that the temperature of the earth depends less on the direct solar heat than on the quality of selective absorption of the atmosphere.

The principles of photography, the radiometer, and the radiophone are next described, though without any new revelations.

The dark lines in the solar spectrum and the spectroscope in its various uses, chemical and astronomical, are expounded. The colour sensation and colour blindness are made the subject of a careful investigation.

Next follows the energy of ether-stress (electrostatics), the energy of ether-vortices (magnetism), and the energy of ether-flow (electrokinetics).

In a concluding chapter follow the relations between light and electricity, and the electro-magnetic theory of light. Maxwell's electro-magnetic theory of light is considered as based upon a firm foundation of experimental fact.

We can scarcely hesitate to pronounce this work the best truly modern manual of physics in our language.

*The Year Book of Science.* Edited for 1892 by Prof. T. G. Bonney, D.Sc., LL.D., F.R.S. London, Paris, and Melbourne: Cassell and Co., Limited, 1893.

So rapid is the advance in these days of the sciences, and so much is the individualisation of each increased, that a work of this kind is needful, not merely for the general reader, but even for specialists themselves, who, immersed each in his own department, are in danger of forfeiting the *esprit d'ensemble.* The object of the editor and his contributors has been to give a condensed view of the progress effected in each department. All the physical and natural sciences are duly considered. The subjects omitted would have been somewhat out of place. Statistics, for instance, is not, strictly speaking, a science, but a method applicable in various sciences; mathematics, in its higher developments, cannot be made interesting to the non-mathematician, and "economy" has not yet reached its scientific stage.

The subject-matter has been selected from trustworthy sources, from the Transactions of Societies of good standing, or from the works of eminent authors. One section only, that on organic chemistry, will be obscure, save to organic chemists themselves.

It may, perhaps, surprise us to find the important subject of bacteriology placed under the head of animal biology, since these ultra-minute beings are now generally regarded as microphytes.

Mr. Thomas Hick, B.Sc., is responsible for a new and, we think, rather needless term "palæobotany."

In the distribution of space chemistry fares well, as it occupies eighty-six pages, of which fifty fall to the lot of organic chemistry. General physics occupies one hundred and thirty-four pages, of which sixty pages are taken up with the popular subject of electricity.

To the biological (animal) section, eighty pages have been assigned, and of this space only four fall to the lot of insects. This is very little if we consider that they are more numerous in species than all the other organic forms taken collectively, and that they exert a most important influence on the life and well-being of mankind.

Experiments made in the hope of rendering animals "immune" to the venom of the cobra by succesive inoculation with minute doses have so far not proved successful. Neither has the strychnine treatment.

The "Year Book of Science" ought to be in the library of every man who wishes to remain intellectually on a level with the age.

# CORRESPONDENCE.

## THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—Allow me to assure Mr. Keyworth that no resolution has been passed by the Institute of Chemistry to erase the letters F.C.S. from the Register; such a resolution was proposed, but was not carried.

The resolution adopted was to the effect that *all* letters should be erased after the name of a Fellow excepting those indicating a Degree or Fellowship of the Royal Society, London. As far as I understand my own language the two resolutions are totally different, and how anyone can maintain that they are identical either in effect or intention passes my comprehension.—I am, &c.,

F. J. M. Page.

Chemical Laboratory, London Hospital, E.,
February 26, 1893.

**Mercuric Chloride as a Reagent for Albumen in Urine.**—E. Spiegler (*Berichte*).—This reagent is rendered more sensitive if applied in the state of a solution of 8 grms. sublimate, 4 grms. tartaric acid, and 20 grms. sugar in 200 c.c. water. If albuminous urine is slightly acidified with concentrated acetic acid and super-stratified upon the reagent, which is specifically heavier, there is formed a sharp whitish ring at the plane of contact. The test is even more sensitive than the ferrocyanide reaction. It is not affected by urinary peptone.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 7, February 13, 1893.

**Study of the Meteorite of the Cañon Diablo.**—Henri Moissan.—The fragments of the meteorite which the author has examined contain transparent diamond, black or carbonado, and a maroon-coloured carbon of very low specific gravity. In certain fragments he has been able to show the presence of graphite in the form of small masses of a fatty aspect. Transparent diamond may therefore be found in other planets besides the earth.

**Meteoric Iron of the Cañon Diablo.**—C. Friedel.—The author has obtained from this meteorite an iron subsulphide, $Fe_5S$, as a brilliant compound, less attackable by acids than iron. There is also a small quantity of a phosphide which has not yet been determined. There occur also nodules of yellow troilite.

**Presence of Graphite, Carbonado, and Microscopic Diamonds in the "Blue Earth" from the Cape.**—Henri Moissan.—The pits in which the South African diamonds are found are filled with a serpentinous breccia containing more than eighty species of minerals, and not containing per cubic metre more than 500 m.grms. of crystalline carbon. The matter of a specific gravity exceeding 3·4 is composed of an amber yellow matter in irregular masses, of carbonado or black diamond, of microscopic diamonds, and of small transparent crystals which do not burn in oxygen, which take the form of elongated prisms, and which do not fluoresce in violet light. The yellow matter contains much iron and has been recognised also in bars of cast iron. The transparent crystals consist chiefly of silica.

**Action of Temperature on the Rotatory Power of Liquids.**—Albert Colson.—The author's experiments show that physical causes may alter the rotatory power of liquids to a considerable extent, even giving rise to changes of sign, and that the chemical constitution does not seem to be the preponderating factor in the value or in the sign of the rotatory power.

**Considerations on the Genesis of the Diamond.**—J. Werth.—The author concludes that the diamond has been formed at a high temperature and under pressure. When formed it has been cooled rapidly. It has been formed in presence of hydrogen more or less carburetted.

**Chlorine Derivatives of the Propylamines, Benzyl amines, Aniline, and Paratoluidine.**—A. Berg.—The author obtains these derivatives by the method which enabled him to prepare those of the amylamines and isobutylamines. He has prepared and examined propylchloramine, propyldichloramine, dipropylchloramine, benzylchloramine, benzyldichloramine, dibenzylchloramine, and certain chloroderivatives of aniline and paratoluidine.

**Dipropylcyanamide and Dipropylcarbodiimide.**—F. Chancel.—The contents of this paper are sufficiently shown by the title.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 1.

**Detection of Glucose in the Blood.**—Pickardt (*Zeit. Phys. Chemie*).—The blood is first freed from albumen and colouring-matter by means of zinc acetate and strongly concentrated. By means of phenylhydrazin and sodium acetate crystals are obtained, which exactly agree with the corresponding compound of glucose.

**Examination of Metallic Iron for Arsenic.**—Otto Sautermeister (*Chem. Zeit.*).—Arsenious acid may be added to 1 grm. of the iron to the extent of 1 decigrm. without giving an arsenical mirror by the Marsh process. An arsenic reaction was obtained in the filtrate with Bettendorff's test (stannous chloride), but not if the filtration is effected after the development of hydrogen has ceased.

**Separation of Toxalbumines.**—Konrad Alt has separated a toxalbumen from the matter vomited by cholera patients. The clear liquids are precipitated with alcohol.

**The Atomic Weight of Cadmium.**—W. L. Lorimer and E. F. Smith.—Already inserted.

## MEETINGS FOR THE WEEK.

Monday, 6th.—Medical, 8.30. (General Meeting).
—— Society of Arts, 8. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "A Convenient Form of Experimental Apparatus for Filtrations and other Determinations," by C. C. Hutchinson. "The Composition of the Petroleum-like Bitumen of Japanese Coal," by Mr. Watson Smith. "The Detection and Estimation of Lead in Citric and Tartaric Acids," by Mr. Warrington.
Tuesday, 7th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "The Functions of the Cerebellum, and the Elementary Principles of Psycho-Physiology," by Prof. Victor Horsley, F.R.S.
Wednesday, 8th.—Society of Arts, 8. "Music in Elementary Schools," by W. G. McNaught.
—— Medical, 8.30. (Annual Dinner).
—— Geological, 8.
—— Pharmaceutical, 8.
Thursday, 9th.—Royal, 4.30.
—— Royal Institution, 3. "The Great Revival—A Study in Mediæval History," by the Rev. Augustus Jessopp, D.D.
—— Society of Arts, 8. "Caste and Occupation at the Last Census of India," by Jervoise Athelstane Baines, I.C.S.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
Friday, 10th.—Royal Institution, 9. "Early Myth and Late Romance," by Sir Herbert Maxwell, M.P.
—— Astronomical, 8.
—— Physical, 5. "The Application of Lagrange's Equations of Motion, with especial Reference to a Perforated Solid in a Liquid," by Dr. C. V. Burton. "On the Magnetic Field of a Circular Current," by Prof. G. M. Minchin, M.A. "On the Differential Equation of Electrical Flow," by T. H. Blakesley, M.A.
Saturday, 11th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Books.—What books would you advise a young chemist to take with him on going out to the gold mines in South Africa?—Onward.

Filters.—I am desirous of information, for lecture purposes, on the subject of filters, and should feel obliged if readers of the Chemical News would tell me where details and diagrams on this subject are to be found.—Water.

THE CHEMICAL NEWS.

VOL. LXVII., No. 1737.

## ON THE ORIGIN OF COLOUR.

### III. IODINE AND IODINE SOLUTIONS.

By WILLIAM ACKROYD.

(Continued from p. 65).

THE element iodine under the influence of heat forms an exception to the rule followed by the bodies so far considered, and its colour scale may prove of use in the study of the class of compounds with isolated absorption-bands. Yellow to reddish brown in thin film it becomes violet on being converted into the vapourous state, and it has two classes of solutions, apparently corresponding to these two states, viz., yellow solutions when the solvent is alcohol or aqueous potassium iodide, &c., and violet solutions when $CS_2$ or $CCl_4$ and certain other bodies are the solvents. I have attempted to make quantitative comparisons between yellow solutions and the solid, and between violet solutions and the gas.

To compare the spectra of a given number of gaseous molecules of iodine with the same number in $CS_2$ solution the following method was adopted. Into small flasks of about 85 c.c. capacity a few grains of iodine were introduced and vapourised in an air-bath with parallel glass sides. The spectrum yielded by one of these being noted for various temperatures, the neck which had been previously drawn out to a capillary tube was now sealed at about 110° C. After removing the flask and allowing the iodine to solidify, the tip of the neck was broken off and the flask filled with re-distilled $CS_2$. All the iodine was now in solution which before existed as vapour, and the light passing through the same parts of the flask on its way to the spectroscope was necessarily acted on by the same number of molecules. With the gaseous iodine there was first observed faint dark lines in the green and yellow. As the quantity of vapour increased there appeared (1) three faint absorption-bands, whose approximate positions in tenth metres I make to be 5456, 5246, and 5047; (2) increase in number of the faint dark lines towards the red, and merging of bands 5047 and 5246 into one. This same quantity of iodine dissolved in $CS_2$ gave one band covering the three gaseous bands, and minus the faint dark lines, its general position being moved a little more towards the violet end of the spectrum than that of the gaseous iodine spectrum.

Now in this case an eye observation notes a change from *red* solid or liquid film to *violet* gas. This iodine colour scale cannot be well introduced into the one we have so far used, as in assuming a violet colour iodine exhibits a distinct line of divergence from the usual order. The element may in this be to some extent typical of a few other bodies, as, for example, some of the organic compounds to which it exhibits points of resemblance, as in dissolving in organic solvents and forming two classes of solutions. It is to some such scale that the rosaniline compounds conform, thus:—

| | |
|---|---|
| Rosaniline .. .. .. | Red, $C_{20}H_{19}N_3$. |
| Phenylrosaniline . .. | Red violet, $C_{20}H_{18}(C_6H_5)N_3$. |
| Diphenylrosaniline .. | Blue violet, $C_{20}H_{17}(C_6H_5)_2N_3$. |
| Triphenylrosaniline .. | Blue, $C_{20}H_{16}(C_6H_5)_3N_3$. |

In passing, one may be permitted to suggest that exact conformity to any scale is not likely to be always observed, as there may possibly be risings and fallings in the colour scale analogous to the rise and fall of melting-points in certain homologous series.

I have made quantitative observations of violet solutions of iodine by the method I described in 1877 (CHEM. NEWS, vol. xxxvi., p. 159), and constructed diagrams where the ordinates are lengths of the solution in c.m. looked through, and the abscissæ are the spectroscopic readings or their equivalents in wave-lengths. Fig. 1 is the diagram obtained for iodine dissolved in $CCl_4$ or $CS_2$ to the extent of 0·00004 grm. per c.c. With 5 c.m. of either of these solutions the green portion of the spectrum appears of decreased intensity, but without any decided band; and this may be put down as the commencement of the absorption. Light passing through 30 c.m. gives a band extending up to D on the one hand, and beyond F on the other with hazy borders. The point of interest which is demonstrated by this quantitative comparison is that the chemical difference of constitution in the two solvents has evidently no tendency to produce differences in the nature or extent of the light absorbed.

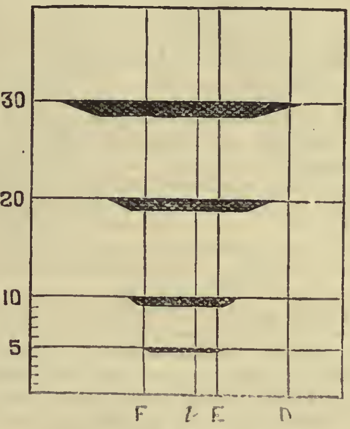


FIG. 1.—Violet solutions.
(0·00004 grm. I per c.c.).

It is self evident that violet solutions of iodine cannot conform to the law of constancy of absorption as set forth in my paper on "Transverse Absorption of Light" (CHEM. NEWS, vol. xxxvi., p. 159). The formula $\frac{c\,s}{m} = t$ may, however, be used for finding the thickness of solid iodine corresponding to the quantity, producing incipient absorption in violet solutions, where $c$ = stratum, length of solution in c.m.; $s$ = strength in grms. per c.c.; $m$ = weight in grms. of 1 square c.m. of solid, 1 m.m. in thickness; and $t$ = thickness of solid plate in m.m. In the case in point we have the commencement of absorp-

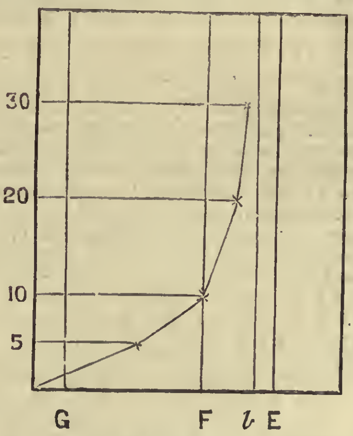


FIG. 2.—Brown solution of iodine.
(0·000062 grm. per c.c.).

tion in violet solutions with a quantity of iodine equal to a film of solid—

$$\frac{5\times 0\cdot 00004}{0\cdot 4948} = 0\cdot 0004 \text{ m.m.},$$

or 4000 tenth-metres thick, which is within the range of the limits of the wave-lengths of light.

As representative of the class of yellow to brown solutions, Fig. 2 gives the curve obtained for a solution of iodine in alcohol containing 0·000062 grm. of the element per c.c. Here the violet end of the spectrum is absorbed, and the absorption increases until, with 30 c.m. of solution, *b* is nearly reached. The thickness of solid film equivalent to the amount of iodine producing absorption up to F is—

$$\frac{10\times 0\cdot 000062}{0\cdot 4948} = 0\cdot 0012 \text{ m.m.},$$

or 12,000 tenth-metres. This figure is a close approximation to Sir John Conroy's estimate, made by other methods, of the thickness of films of iodine, varying in colour from deep brownish-red to brown ("The Absorption Spectra of Iodine," *Phil. Trans.*, vol. xxv., p. 51 *et seq*).

The foregoing comparisons lead me to place the various appearances of iodine and its solutions in the following order of evolution:—

| | | |
|---|---|---|
| 1. | Yellow to brown | Solid and liquid films. |
| 2. | ,, ,, | Solutions in alcohol, &c. |
| 3. | Violet | Solution in $CS_2$, &c., one absorption band. |
| 4. | Violet | Vapourous iodine, three absorption-bands + fine lines. |

As one may regard this order of change as being in large part due to disintegration of molecular masses, I have made an attempt to find out the relative amounts of heat absorbed due to solution, but so far unsuccessfully, this being owing to the fact of so small an amount of iodine being dissolved that an error of a tenth of a degree C. rendered the results entirely valueless.

Halifax, Feb. 20, 1893.

# ACTION OF CARBON UPON SOLUTIONS OF SALTS OF THE RARE EARTHS.

By K. HOFMANN and G. KRÜSS.

Porous carbon, especially bone-black, is well known to possess the power of absorbing certain substances whether from the air or from a solution into which it is introduced. In most cases this depends upon the fact that the surface attraction here reaches a perceptible degree of efficacy in consequence of the great extension of surface, although no chemical process occurs. But in other cases, chemical reactions may be recognised. Thus, *e.g.*, porous charcoal partially precipitates on its surface hydroxides from the saline solutions of feebly basic oxides such as those of iron and aluminium, whilst free acid is split off.

Accordingly we examined whether the behaviour of the rare earths was similar to that of the oxides just named, and whether the weaker earths are not liable to this action of carbon in a greater degree than the more powerful bases, thus leading to a partial separation.

As, however, animal charcoal contains calcium phosphate in large quantity, which must have a disturbing effect, the attempt was made to eliminate it by means of dilute hydrochloric acid; which was only partially successful, as on igniting the charcoal there always remained a considerable incombustible residue. A preminary experiment was, however, made with animal carbon approximately purified in this manner, and the earth separated by treatment with charcoal was subsequently most carefully purified. (See *Zeit. Anorganische Chemie*, iii., 48 and 49).

The solution of the earthy chloride used was freed from free hydrochloric acid as far as possible by evaporation; the clear solution was mixed with ammonia, until on heating there remained a small permanent precipitate, which was filtered off.

The bone-black, previously ignited, was put into the clear filtrate, containing in 200 c.c. 3 grms. of earth, using 10 grms. of carbon to 1 grm. of earth. After heating on the water-bath for two hours and allowing the liquid to cool, it was filtered, and the carbon was washed with distilled water until the filtrate no longer gave a precipitate with ammonia. The carbon was then incinerated, the earth dissolved out of the ash by warming with hydrochloric acid, the solution precipitated with oxalic acid, the oxalate ignited, and the earth then once more purified in the same manner as in the former determinations of the equivalents (iii., 48). The earth separated by the carbon contained a $\overset{\text{III}}{R}=155\cdot 94$; the portion not precipitated gave the atomic weight 138·7.

To obtain unobjectionable results it was necessary to use a carbon containing no phosphoric acid, as the presence of the latter substance may have occasioned the above difference of the atomic weights. But the complete removal of phosphoric acid from earthy substances is well known not to be easy. Such a carbon was prepared by dissolving 150 grms. cane-sugar and 75 grms. potassium carbonate in water, evaporating down the solution, and heating the residue to 600° for eight hours, with exclusion of air. The mass obtained was pulverised, lixiviated with water, and finally washed upon a filter with dilute hydrochloric acid until every trace of potassium carbonate was removed. This carbon, used in the manner above described, separated from a material, $\overset{\text{III}}{R}=116\cdot 8$, a portion which, on determining its combining weight, was found to contain $\overset{\text{III}}{R}=134\cdot 4$.

Hence it is demonstrated that a partial separation of the rare earths can be effected by means of porous carbon. But the quantities thrown down by the earth are rather trifling, *e.g.*, 0·05 grm. from 2 grms. earth on employing 8 grms. carbon. Hence it is not advantageous to work up a material of rare earths on this principle from the beginning.

The use of a porous carbon seems, however, very advantageous for separating from a rare earth small quantities of more feebly basic oxides, *e.g.*, yttria from an admixture of more feebly basic gadolinite earths, which readily cause it to take a slight yellowish colour. Thus from an yttria material, which, according to its analysis, contained a $\overset{\text{III}}{R} = 93\cdot 03$ ($\overset{\text{III}}{Y} = 90$) there was obtained by a single treatment with carbon an earth the equivalent of which was found to be $\overset{\text{III}}{R}=96$, a result which could not be obtained from this material in a single operation even by precipitation with aniline.

Porous carbon may therefore be used as a good separating agent in the final purification of the rare earths. It seems also advisable to examine the behaviour of an earthy salt with porous carbon if we wish to be satisfied of the unitary character of a rare earth supposed to be homogeneous.—*Zeit. Anorganische Chemie*, iii., p. 89.

**On Aconitine.**—A. Ehrenberg and C. Furfurst (*Jour. Prakt. Chemie*).—The pure base melts at 193° to 194°, but very minute traces of a decomposition product depresses the melting point by 10°.

## BEHAVIOUR OF SOME METALS WITH GASES.

By G. NEUMANN.

The portion of this investigation relative to hydrogen has been executed by the author in conjunction with F. Streintz. Their attention was drawn to the question by the view that lead as the negative plate of a secondary element is capable of occluding hydrogen.

A proof for the correctness of this view could not be obtained by direct electrolytic experiments, as the arrangement of the experiment proved too difficult. Better results were obtained on allowing pure, dry hydrogen to pass through melted lead in a U-tube.

After the gas had been passed for a considerable time, the excess was driven out by nitrogen. Oxygen was then passed through, and this again was expelled by dry air. The water formed by the action of oxygen was received in calcium chloride tubes and weighed, and the quantity of hydrogen absorbed by the metal was thus calculated. In two experiments which could be regarded as successful the result was in one case 0·15 times the volume of the metal, and in the other 0·11 times. Hence the occluding power of lead for hydrogen seems demonstrated.

The next experiments were made with palladium. This metal, as is well known, occludes hydrogen very greedily. The experiments, as well as those with other metals still to be mentioned, were executed in an analogous manner to those on lead, *i.e.*, the dry hydrogen was passed over the heated metal. The metal was used as palladium black. Hydrogen was absorbed to the extent of 502·35 times the volume of the metal.

Platinum was examined as platinum sponge and platinum black. The latter acts more energetically, is raised to redness by absorption without the application of external heat, as is palladium by the absorption of oxygen. Platinum sponge occludes 49·30 times its volume of hydrogen. This figure varies considerably from that found by Graham. For an explanation of this difference we must refer to the original.

Gold occludes relatively much hydrogen; the action of oxygen upon the metal charged with hydrogen is not very strong. In two experiments there were obtained respectively, 46·32 and 37·31 times the volume of the metal. Here also the values were decidedly higher than those ascertained by Graham. The latter used gold from so-called assay-rolls, whilst the authors employed a preparation obtained by precipitating the chloride with oxalic acid.

Silver absorbs, according to the author's experiments, no hydrogen, whilst, according to Graham, silver wire occludes 0·211 times its volume. Aluminium absorbs 2·72 times its volume of hydrogen in thin sheets previously purified.

Iron in a state of fine division aborbs 19·17 times its volume. Copper occludes about four and a half times its volume.

Nickel, which in its chemical properties is intermediate between copper and iron, behaves similarly in its occlusive power for hydrogen. It occludes 17·57 volumes.

The absorption of hydrogen by cobalt is rather large, and the metal when charged with hydrogen becomes incandescent in a current of oxygen.

The occlusive power of some metals for hydrogen decreases on a repetition of the experiments. The authors explain this in the noble metals by an increase of density. This occurs according also to Graham. Copper and nickel on a repetition of the experiment show the same occlusive power. In the case of iron and cobalt, which behave like the noble metals, the authors have not yet found any explanation.

Neumann has examined the behaviour of the precious metals with oxygen by a method analogous to that above described.

The metals were ignited for some hours in pure oxygen, two calcium chloride tubes were then attached before the occlusion tube, and a potash apparatus to observe the rapidity of the gas; the oxygen was displaced by air, and this, again, after cooling, by nitrogen. After the current has passed for half an hour, hydrogen was introduced and heat was applied. The water formed was received in the calcium chloride tubes, which were weighed after they had been successively traversed by nitrogen and air.

Silver on being thus treated absorbed 4·09 vols., which does not agree badly with Graham's result, according to which from 6·15 to 7·4 vols. were absorbed.

Gold absorbed 48·49 vols. of oxygen, whilst Graham observed no absorption. Neumann believes that this difference may be explained by the temperature of the experiment.

In case of platinum, concerning the absorptive power of which for oxygen there is much discrepancy among former observers, Neumann found occlusion of 77·14 vols. With palladium the author found a formation of suboxide, since the residue after treatment with oxygen contained 6 99 per cent, whilst $Pd_2O$ contains 7·33 per cent.

Neumann considers that the absorptions of oxygen depend on a power of the metals to become oxidised at about 450°, the temperature of the experiment.—*Zeit. Anal. Chemie*, vol. xxxii., p. 72.

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## DETERMINATION OF CALCIUM TARTRATE.

By CH. ORDONNEAU.

We take 20 grms. calcium tartrate, an average sample, pulverise them finely in the mortar, and add 20 c.c. of commercial hydrochloric acid at 20°, diluted in 100 grms. of water. The solution may be promoted by heating to ebullition. We make up 202—203 grms., according to the quantity of the insoluble matters, and filter. We take 50 grms. of the solution when cold, and pour it into a flask holding about 90 c.c. We add 2 c.c. of solution of citric acid at 25 per cent, and then 10 c.c. of solution of calcium acetate at 25 per cent (25 grms. calcium acetate and water to make up 100 c.c.). We agitate strongly, when crystals of calcium tartrate form after a few minutes. We then add 5 c.c. more of the same solution of calcium acetate, agitate, and allow it to settle for fifteen or thirty minutes. All the tartar is precipitated in a pure state.

We pour the whole upon a plain filter 9 c.m. in diameter, detach the tartar adhering to the flask with a slender piece of curved wood, wash the flask and the tartar from the filter with 30 c.c. of water in several portions.

The filter is then opened and laid on a plate of copper or sheet-iron above a water-bath. The paper dries enough to permit the separation of the tartar, which is transferred to a round nickel capsule 9 c.m. in diameter. The filter is dried completely, the tartar is detached and added to that in the capsule.

The capsule is then placed on the water-bath so as to dry the calcium tartrate completely. The desiccation is promoted by stirring the mass with a very pliable spatula. We cease when the tartar, which forms clots as long as it is moist, begins to flow like dry sand. At this moment we wipe the capsule and weigh the tartar obtained.

The result found, multiplied by twenty, gives the standard of the tartar if we have operated upon 5 grms. of substance. To this must be added 2 per cent to compensate for the loss on the filter and the solubility of calcium tartrate.

The exact moment of drying must be seized when the calcium tartrate contains $4H_2O$. Each additional minute causes a loss of 0·10 per cent of tartar, but as the point is easy to seize (for it occurs suddenly on stirring the substance), there is no error in this respect beyond 0·20 per cent, which may be neglected.

By this process there are formed calcium tartrate, calcium chloride, and free acetic acid, which has no action on calcium tartrate. As the precipitation of the tartar is always effected in a very acid liquid, malic acid, if it is present, remains in solution and does not falsify the results.

The object of the citric acid is to dissolve the aluminium phosphate, which forms a lake with the colouring matter, and which the acetic acid does not dissolve. It is also without action upon calcium tartrate. It is preferable to precipitate in two portions, since the crystals of tartar are thus coarser, which renders it easier to seize the exact moment when the moisture is expelled.

If we wish to determine the total acidity of any tartar we must operate in the same manner, adding 25 c.c. of solution of calcium acetate in two portions. This quantity is sufficient for 5 grms. pure potassium bitartrate, and consequently the process is general.

The calcium tartrate must be washed, collected, and weighed. We have then to add 2 per cent to the amount found, and on multiplying the calcium tartrate by 0·576 we have the value in tartaric acid.

*Second Process.*—We take 50 grms. of the solution of tartar, which is poured into a porcelain capsule and heated to ebullition. We add then some drops of solution of phenolphthaleine, and then gradually, and with continual stirring, a clear milk of lime which has been strained through silk. The source of heat is extinguished or removed as soon as "bumping" sets in; the saturation is continued, giving the calcium tartrate time to subside after each addition of lime, and ceasing when neutrality is reached, which requires about five minutes. We add then to the liquid 2 c.c. of the citric solution at 25 per cent, stir, and allow it to subside. After some minutes the temperature is 50° to 60°, when we decant, pour the tartar upon a plain filter of 0·09 metre, and wash with 30 c.c. of water.

The calcium tartrate is dried as above, taking care not to break the filter. To the result obtained we add 4 per cent for the solubility of the substance in the liquid and the loss on the filter. Even if the quantity of malate exceeds 20 per cent, which is a very rare case, we need add only 3 per cent for accuracy, as the solubility is then lower. The quantity of malate is found by the deficiency of the result plus the insoluble matters to make up 100. On operating thus on pure calcium tartromalate, or on a mixture of the two salts in equivalent proportions, we find 99·50 per cent of calcium tartrate almost free from malate.

This process has the advantage of serving for industrial refining. In place of adding citric acid we leave a slight acidity, which dissolves the alumina and the phosphates. The tartar obtained is pure if the liquid is decanted whilst luke-warm, for complete refrigeration precipitates the calcium tartromalate to the extent of about 10 per cent of the tartar operated upon. This salt is collected and utilised in a fresh operation.—*Bull. Soc. Chim. Paris*, Series 3, ix.—x., p. 68.

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# THE GREENE-WAHL PROCESS FOR MANUFACTURING MANGANESE AND ALLOYS OF MANGANESE FREE FROM CARBON.*

By F. LYNWOOD GARRISON.

The great objection to the use of ferro-manganese in the manufacture of steel has been its invariable association with considerable quantities of carbon, causing, when it is added to a low carbon steel to produce manganese-steel, a hardening of the steel, whatever may be the action of the manganese. There would seem to be commercial advantages in producing a ferro-manganese free from carbon, so that the steel to which it was added would receive the beneficial effect of the manganese without the carbon contents being increased. Mr. Garrison believes the question of producing a ferro-manganese free from carbon to be solved by Messrs. Greene and Wahl.

The first attempt to produce metallic manganese in considerable quantities seems to have been made by Hugo Tamm in 1872. Native dioxide of manganese was heated with powdered charcoal or lampblack and oil in the presence of a powdered siliceous and fluor-spar flux. The manganese obtained having contained an appreciable amount of carbon, Tamm made attempts to remove this by fusing the metal under a layer of manganese carbonate. Tamm claimed to have made a metal having the composition — Manganese, 96·9; Fe, 1·05; carbon, 0·95; and other elements, 0·10; from a pyrolusite containing 50·5 per cent manganese and 3·5 per cent iron. The resultant metal, after refining this product under the fused coating of manganese carbonate, contained—Mn, 99·91; C, 0·025; Si, 0·015; Fe, 0·05. These results have not been confirmed, however, by later experimenters, and they are doubted. Messrs. Greene and Wahl's first experiments were made for the purpose of testing the correctness of Tamm's assertions, and were unsuccessful in decarbonising the metal to any extent. They then became convinced that the first step in such a process should be the removal of the iron combined with the manganese. After abandoning magnetic and electro-chemical methods, they found that nearly all the iron of rich manganese ore could be removed by digesting the pulverised ore with 30 per cent sulphuric acid, the manganese remaining practically unaffected. The percentage of iron can be reduced from 5 or 6 per cent to a few tenths in a few hours, and the waste acid can be utilised in making ferrous sulphate.

The reduction of the purified ore then became a puzzling problem; it was found impossible to produce manganese containing less than 6 per cent carbon by reduction with carbon, and this high percentage of carbon could not be removed in the later operations by fusion with an oxidising agent. Messrs. Greene and Wahl believe that a complete reduction of any manganese oxide by carbon yields, not a manganese, but a carbide having the definite form $Mn_3C$. For this reason manganese free from carbon cannot be reduced in the electrical furnace or in graphite crucibles. Experiments with the electrolysis of the fused baths of manganese chloride and manganese fluoride were futile, and it became evident that a reduction, in the entire absence of carbon, was necessary for the solution of the problem. Moreover, the compound to be reduced should be one of the oxides of manganese, as the use of halogen compounds on a commercial scale and the reduction by sodium were precluded by reason of the cost of their manufacture.

Messrs. Greene and Wahl, having determined that the reduction by means of metallic aluminum, which had been barely experimented with by Michel, Wöhler, Levy, and Langley, was the proper method, they soon found that neither clay nor graphite crucibles could be used in the operation—the graphite for reasons mentioned before, and the clay because of the energetic action of the aluminum upon the silica; experiments yielding a siliceous manganese containing in some instances as high as 12 per cent silicon. Calcined magnesite, however, was found to answer the purpose, and a graphite crucible lined with this afforded excellent results. In producing this pure manganese, the manganese dioxide is reduced to monoxide by heating in a stream of reducing gas. It is then mixed with granulated aluminum and with a flux of lime and fluor-spar. The mixture is then placed in the magnesite-lined black-lead crucible, and placed in a furnace commonly employed in melting brass. When the contents have reached a bright red, the aluminum begins its energetic reducing action upon the manganese monoxide, and in a few minutes the reaction is complete. The heat liberated liquefies the contents of the crucible,

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* A Paper read before the American Institute of Mining Engineers, Montreal Meeting.

and brings them to a white heat. The inventors state that they have obtained a yield as high as 2·84 parts of manganese per unit of aluminum, equal to 94·5 per cent of the theoretical yield. The following is the reaction that occurs :—$Al_2+MnO=Al_2O_3+3Mn$. The metal obtained is dense and homogeneous, with a steel-grey colour and a pinkish to reddish bronze tint. It is hard and brittle, having an irregular fracture. The specific gravity varies between 7·26 and 7·38, or 7·32 on an average. Its average composition is Mn, 96·5; Fe, 2; Si, 1·5. It retains but the slightest trace of aluminum.

In operating a small plant capable of producing about 2 tons of manganese per week, the inventors state that 1560 lbs. of aluminum and 5 tons of manganese ore will be required. Basing their calculations of the present market value of aluminum at 55 c. per pound, and manganese ore at 40 dollars per ton, they find that the manganese will cost about 7·60 dollars per long ton, or about 34 cents per pound.

As yet the process has been conducted on a laboratory scale only, but it would seem to have many possibilities. —*Engineering and Mining Journal.*

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 105).

### *Erdmann and Marchand's Work.*

THERE is no need of our here repeating what was said in the prefatory note (*ante*). We therefore pass at once to an account of our experiments on the dehydrating powers of chloride of calcium and caustic potash. Our apparatus consisted of the following successive communicating parts :—

I.—A Pisani gasholder, containing a little over 12 litres of air, shut up over dilute solution of caustic potash or soda, followed by—
A.—A large tower charged with fragments of recently fused caustic potash.
B.—A tared U-tube, charged with the same reagent.
C and D.—Two U-tubes, charged with vitrioled pumice; both tared.
E.—A wash bottle, containing water.
F and G.—Two U-tubes charged with fragments of recently fused chloride of calcium; both tared.
H.—A U-tube, charged with vitrioled pumice; tared.
K.—A similar tube, untared.

The U-tubes intended for the determination of the weights of absorbed matter were all tared, not with weights, but with similar tubes of as nearly as possible the same displacement. Each tare-tube contained a quantity of selenite adjusted so that it displaced very nearly the same volume of air as the chloride of calcium or caustic potash in the working tube. Our U-tubes were all of that now popular kind in which the gas enters and goes out through laterally-soldered-in short tubes, and the orifices are provided with perforated ground-in hollow glass stoppers, so that one can close either or both sides by a turn of the stopper, or open them to admit the respective current of gas.†

The necessary tarings having been effected, and the apparatus put together, the air from the Pisani was turned on and made to pass through the apparatus at a suitable rate, until a sufficient volume had accumulated in the graduated Pisani bottle. The following diagram will facilitate the reading of the tables of results :—

| Pisani | KHO | KHO | $H_2SO_4$ | $H_2SO_4$ | Water | $CaCl_2$ | $CaCl_2$ | $H_2SO_4$ | $H_2SO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| I. | A | B | C | D | E | F | G | H | K |

*First Set.*

| | Experiment— | | | |
|---|---|---|---|---|
| | I. | II. | III. | |
| Temperature .. | 12—14° | 12·7—14° | 14—16° | |
| Volume of air, .. | 12 | 2·5 | 11 | litres. |
| which passed in | 4 | 1·25 | 2 | hours. |
| KHO, B, gained .. | 0·6 | 0·15 | −0·2 | m.grm. |
| Vitriol, C, gained . | 1·35 | 0·15 | 0·1 | ,, |
| *After Water.* | | | | |
| $CaCl_2$, F, gained.. | — | — | 70·4 | m.grms. |
| $CaCl_2$, G, gained.. | 0·2 | nil | 12·8 | ,, |
| Vitriol, H, gained . | 2·2 | 0·45 | 2·5 | ,, |

From these numbers we see that the caustic potash tower dehydrated the air so completely that the potash U-tube following it had little or nothing to do; and, assuming oil of vitriol to be a perfect dehydrator for gases, that in experiments II. and III. at least, the caustic potash dehydrated the air as good as completely. The fused chloride of calcium dehydrated the moist air coming from E so completely, that only 0·183, 0·180, 0·227 m.grm. of water were left in every litre of air. In a corresponding experiment by Fresenius the residuum of water amounted to 0·97 m.grm. per litre. (See p. 179 of his memoir.) Fresenius says that his chloride of calcium was fused and put into the tubes while still hot. This is exactly what we did, except that we allowed our preparation to cool before filling the tubes with it; hence we are at a loss to explain why our tubes worked so much better than his. But we had no doubt in our mind that Fresenius's chloride of calcium was a fair preparation, and took it to be a fair presumption that Erdmann and Marchand's preparation was no better than that of Fresenius. We therefore spoiled our chloride of calcium expressly by passing moist air through it until it had gained 130 m.grms. in weight, and then resumed our experiments. In experiments IV., V., VI., the wash-bottle E and the two chloride of calcium tubes were immersed in a water-bath kept at 25°. In experiments VII. and VIII. only the wash-bottle and the first chloride of calcium tube were kept at 25°, the second $CaCl_2$ tube was not artificially heated or cooled.

*Second Set.*

| | Experiments. | | | | | |
|---|---|---|---|---|---|---|
| | IV. | V. | VI. | VII. | VIII. | |
| Temp. of air.. | 13·5-16·5 | 13-16 | 11·5-15° | 11-15° | — | |
| *Temperature of water kept at 25° throughout the series.* | | | | | | |
| Volume of air .. | 10 | 10 | 10 | 10 | 10 | litres. |
| Time .. .. .. | 2 | 2·25 | 2·25 | 2·25 | 2 | hours. |
| Gain of B.. .. | 0·6 | 0·5 | 0·3 | 0·5 | * | m.grm. |
| Gain of C.. .. | 0·5 | −0·1 | 0·3 | 0·3 | * | m.grm. |
| *After Water.* | | | | | | |
| Gain of F.. .. | 122·8 | 129·6 | 114·8 | 125·0 | * | m.grm. |
| Gain of G.. .. | 14·0 | 9·3 | 2·9 | 6·6 | 2·0 | ,, |
| Gain of H.. .. | 6·3 | 5·0 | 7·8 | 6·0 | 5·0 | ,, |
| Hence, 1 litre of chloride of calcium dry air contains— | | | | | | |
| Of water .. .. | 0·63 | 0·5 | 0·78 | 0·60 | 0·5 | m.grm |
| While 1 litre of KHO dry air contains— | | | | | | |
| Of water .. .. | 0·05 | 0·0 | 0·03 | 0·03 | * | m.grm. |

* Not determined on account of want of time.

We deem it worth while to state that, even after the eighth experiment, the chloride of calcium in the outlet limb of tube G was still glassy in appearance, and that even that in the inlet end was not visibly spoiled. What we mean to say is that it would have passed in any laboratory for fair enough chloride of calcium for ordinary work. From our experiments and Fresenius's conjointly, we derive the conviction that a gas which has been dried by means of apparently well-conditioned chloride of

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* *Proceedings of the Philosophical Society of Glasgow.*

† Both remarks apply to the vast majority of the respective experiments reported on in the preceding section.

calcium may contain as much as 1 m.grm. of water per litre. Fused caustic potash, on the other hand, dries a gas quite completely. We assert this the more confidently, as our second series of syntheses (which came long after the experiments now under discussion) proved to us again and again, that a gas which has passed over a long enough column of recently fused caustic potash *gives up no water even to phosphoric anhydride.*

On these facts we base the following hypothesis concerning Erdmann and Marchand's work:—In their last four experiments (and only these need to be taken into account), the hydrogen which entered their reduction-tube was free of any kind of oxygen, because they avoided the use of oil of vitriol as a dehydrating agent, and passed their gas over red-hot metallic copper before it reached the final dehydrator. But the surplus hydrogen which passed through the reduction-tube at the end of the experiment, and the air which followed it, carried away with them an appreciable weight of vapour of water, because there was only a chloride of calcium tube at the outlet of the water receptacle to catch it. Assuming, now, that they used (let us say) 3 litres of surplus hydrogen and 3 litres of air, for every 8 grms. of oxygen used as oxide of copper, and that their chloride of calcium was at a par with Fresenius's as a dehydrator, about 6 m.grms. of the water which they produced failed to find its way to the balance. Now, their reported water-weight was almost exactly = 9·000 grms. per 8 grms. of oxygen; hence their total water actually produced was equal to 9·006 grms.; and hence their real value for H (if $O=16$), is 1·006, and not 1·000.

Dumas produced too much water, but may have underdetermined its weight by forgetting the vacuum reduction. Erdmann and Marchand produced the correct amount of water and weighed what they had on the balance correctly, but they lost some of their water before it came to the balance.

We will now pass to our own first series of syntheses which, as may be remembered, was made before we had discovered the reducing action of vitriolised pumice on hydrogen gas.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, February 16th, 1893.*

Prof. A. Crum Brown, F.R.S., in the Chair.

It was announced that the following changes in the Council were proposed by the Council:—

As President: Professor H. E. Armstrong, *vice* Professor Crum Brown.

As Vice-Presidents: Dr. E. Atkinson and Mr. C. O'Sullivan, *vice* Professor Hartley and Mr. Warington.

As Secretary: Professor Dunstan, *vice* Professor Armstrong.

As ordinary members of the Council: Messrs. C. F. Cross, Bernard Dyer, D.Sc., Lazarus Fletcher, M.A., and W. A. Shenstone, *vice* Mr. H. Bassett, Professor Ferguson, Mr. J. Heron, and Mr. S. U. Pickering.

Messrs. Holland Crompton, T. S. Dymond, and Dr. T. A. Lawson were appointed to audit the Society's accounts.

Ordinary certificates were read for the first time in favour of Messrs. Lawrence Augustus Baine, Dipton, Lintz Green, Newcastle-on-Tyne; George Clayton, School of Pharmacy, 100, Burlington Street, Manchester; Robert George Grimwood, 41, Lady Margaret Road, St. John's College Park, N.W.; Alfred Rowland Gower, 39, Stafford Street, Barrow-in-Furness; Hooper Albert Dickinson Jowett, 3, Fern Bank, Lancaster; Herbert Lloyd, Philadelphia, U.S.A.; Edmund George Lamb, 29, Great Cumberland Place, W.; James Mason, Cambois, Blyth, Northumberland; Henry John Monson, 15, Palace Street, Buckingham Gate, London, S.W.; William Henry Oates, Broomhall Park, Sheffield; S. Parrish, 15, Fenton Street, Woodhouse Lane, Leeds; Frank P. Vandenbeigh, B S., M.D., Buffalo, New York; A. F. Watson, 11, York Place, Edinburgh.

The following were duly elected Fellows of the Society: — John Pedrozo D'Albuquerque; William Thomas Boone; John Edwin Brockbank; Edward Brooke; George Davey; Daniel O. Sydney Davies; Charles Dreyfus, Ph.D.; Samuel Felix Dufton, B.A., D.Sc.; Francis P. Dunnington; Alexander Stanley Elmore; Frederick George Fuller; Albin Haller; George Nevill Huntly; Arthur John Heath; Wesley Lambert; Charles M. Luxmore; Fred. Marsden; Herbert Bloome Mole; William J. Martin, jun., M.D.; Robert Henry Owen; Charles Platt, A.C.; James Robert Thackrah, M.A., Ph.D.; Charles Thomas Tyrer; John William Towers; John Charles Umney; Henry C. White; Willoughby Walke; Charles E. Waite; William Ernest Wheeler.

Of the following papers those marked * were read:—

*113. "*Note on the Preparation of Platinous Chloride, and on the Interaction of Chlorine and Mercury.*" By W. A. Shenstone and C. R. Beck.

In a paper read before the Society last year (*C. S. Trans.*, 1892, 445) we gave the results of the analysis of the gas evolved on igniting various specimens of platinous chloride *in vacuo*, showing that in every case very sensible quantities of hydrogen chloride and oxygen were present. The greatest amount of impurity was found in a specimen derived from the salt prepared by heating hydrogen platinichloride *in vacuo* in a tube containing solid potash, as recommended by Pigeon (*Compt. Rend.*, 1892). This last fact and Pullinger's description of his method of preparing anhydrous platinic chloride (*C. S. Trans.*, 1892, 422) led us to conclude that probably a more satisfactory product, at any rate as a source of chlorine, would be obtained by heating hydrogen platinichloride at a high temperature in a current of dry hydrogen chloride.

*Experiment* I. — Some hydrogen platinichloride was heated at the boiling-point of mercury in a current of dry hydrogen chloride during fifteen hours, and the hydrogen chloride was then displaced by dry air. A part of the product was ignited *in vacuo*, and the gas which was given off was examined in the manner previously described (*loc. cit.*). We found that the residue from the action of mercury only amounted to 0·156 per cent. This residue was partly soluble in water as before. The gas made in this way therefore contained 99·84 per cent of chlorine.

*Experiment* II.—A portion of the product of the first experiment was heated in a current of dry hydrogen chloride at about 500° during many hours by placing it in a glass tube surrounded by a well-fitting glass jacket immersed in a bath of molten nitre; at the end of the operation the hydrogen chloride was expelled by means of dry air. The process was rather difficult to carry out, as the complete decomposition of the salt easily takes place if the temperature too much exceeds the melting-point of silver chloride, some decomposition occurring even at that temperature.

A portion of the product of this experiment was placed in a glass tube, which was then exhausted as in our previous experiments; it contained no drying material, but both the tube and its contents were heated to drive off moisture. Chlorine was generated from the chloride by igniting it *in vacuo*, and the residual platinum having been removed, one end of the tube was broken under mercury. Although we had intentionally neglected to dry the gas, we were at once struck with the fact that the action between this sample of chlorine and mercury was decidedly less active than in the case of any of the specimens previously examined, and when the action of mercury was at an end so little residue was left that its analysis by the method formerly described seemed useless. The part of the narrow tube which had contained the residual gas was therefore cut off and calibrated: it was thus found that the residue amounted to only 0·06 per cent of the gas taken. The residue was partly soluble in water.

We have not determined the total chlorine in the platinous chlorine made in this way, as we do not think it consisted of pure platinous chloride; it probably contained a little platinum, but as a source of chlorine it seems to be very superior to the product of the more familiar processes.

We have previously suggested that the marked activity of even the most carefully dried chlorine towards mercury is probably due to the presence of impurities in the gas. The sluggish action of chlorine and mercury observed in our second experiment, in which the chlorine employed, though not quite dry, contained much less hydrogen chloride and oxygen than any that we have previously examined, is therefore interesting and suggestive.

Shortly after the publication of our former paper on this subject, Professor Victor Meyer called our attention to the fact that in his later experiments on the density of chlorine he assured himself that the other gases present in the chlorine employed were insufficient in quantity to materially affect the chief conclusion he drew from his results (*Ber.*, xiii., 1721). We are anxious to mention this, although we made no direct reference to the subject in our paper, as one of our remarks might very possibly be supposed to imply the contrary.

### Discussion.

Mr. Groves having asked whether the authors had made any further experiments in the direction of fractionally evaporating liquid chlorine, Mr. Shenstone, in reply, stated that by fractionating the liquid they had obtained chlorine which, when tested by mercury, was found to be almost as nearly pure as that obtained from platinous chloride. This chlorine, however, acted rapidly on mercury, even after it had been highly heated, and he was inclined to suspect the presence of traces of oxy-compounds in it. It was worth while mentioning that recently roasted chlorine does not appear to cause the adhesion of mercury to glass in anything like the same degree that ozone or unroasted chlorine does. Whether this is due to a change in the gas or to a change on the surface of the glass he could not say.

*114. "*The Action of Phosphoric Anhydride on Fatty Acids.*" Part III. By F. Stanley Kipping, Ph.D., D.Sc.

Results of an investigation of the behaviour of some of the fatty acids with phosphoric anhydride have been communicated to the Society in previous papers (*Trans.*, 1890, 532, 980); it is now shown that caprylone, $(C_7H_{15})_2CO$, nonylone, $(C_8H_{17})_2CO$, and myristone, $(C_{13}H_{27})_2CO$, can be easily prepared from the corresponding fatty acids and phosphoric anhydride.

The hydroximes of these ketones, the secondary alcohols obtained from the ketones by reduction, and the acetyl derivatives of some of the alcohols have been prepared and characterised, and are described in the papers. It is also shown that mixed ketones of the general formula R·CO·R′ are produced when a mixture of two fatty acids is treated with phosphoric anhydride at a moderately high temperature; the mixed ketone is accompanied by two simple ketones, just as is the case when a mixture of the barium salts of two fatty acids is submitted to dry distillation.

The question of the existence of isomeric modifications of the hydroximes of fatty asymmetrical ketones is briefly referred to.

It would appear from the results described in this paper and from those already recorded, that treatment with phosphoric anhydride is one of the simplest and most rapid methods by which a fatty ketone of the general formula $(C_nH_{2n+1})_2CO$ can be prepared from a fatty acid $(C_nH_{2n}O_2)$, the product being easily isolated and the yield fairly good, especially in the case of the higher acids.

*115. "*Regularities in the Melting-points of Certain Paraffinoid Compounds of Similar Constitution.*" By F. S. Kipping, Ph.D., D.Sc.

Having obtained considerable quantities of many of the fatty ketones $(C_nH_{2n+1})_2CO$, the author was able to prepare and characterise their more important derivatives; *e.g.*, various members of the series of hydroximes $R_2C{:}NOH$, secondary alcohols $R_2CH{\cdot}OH$, and ethereal salts $R_2CH{\cdot}OAc$.

Attention is drawn to certain regularities observed on contrasting the melting-points of these compounds; it is also pointed out that the melting-points of all ketones of the general formula $C_nH_{2n}O$ cannot be calculated by means of the formula suggested by Mills (*Phil. Mag.*, 1884), inasmuch as isomeric ketones frequently melt at different temperatures.

### Discussion.

Mr. A. R. Ling drew attention to the similarity in the melting-points of many chlorinated derivatives of *p*-benzoquinone and of the corresponding quinols and their diacetyl derivatives as compared with those of the analogous bromo- and chlorobromo-compounds. The agreement seems to be wanting in the para-dihalogen derivatives, but in all other cases it is sufficiently close to be remarkable. The displacement of chlorine by bromine is usually attended by a rise in the melting-point, but meta-chlorobromoquinone and its derivatives melt at slightly lower temperatures than the corresponding dichloro-compounds. Only two iodoquinones are known, but their melting-points do not exhibit the least similitude as compared with those of their analogues.

116. "*Some Relations between Constitution and Physical Constants in the case of Benzenoid Amines.*" By W. R. Hodgkinson and Leonhard Limpach.

A study of the formyl and acetyl derivatives of certain homologues of aniline shows, amongst other things, ($\alpha$) that the entry of alkyl groups into the nucleus affects the melting- and boiling-points in a regular manner; ($\beta$) that the conversion of formyl into acetyl also involves an alteration in physical properties in extent the same as that produced by introducing $CH_3$ into the nucleus in an *ortho-* or *para*-position relatively to the amido-group; and ($\gamma$) that the same (or any ?) alkyl group entering the nucleus in the meta-positions has *no* effect on melting- or boiling-point. Several numerical regularities are also apparent.

Thus, taking the melting-points of the methylamido-benzenes as first examples:—

| | | | |
|---|---|---|---|
| Formanilid .. .. | 46° | Acetanilid .. .. | 114° |
| Formylxylid .. | 76 | Acetxylid .. .. | 144 |
| Difference .. | 30 | Difference .. | 30 |

That the introduction of methyl into the meta-position has no influence on the melting-point is shown by the fact that the following substances melt at the same temperature within a degree:—

| | |
|---|---|
| Acetmesidid .. .. .. | NHAc : Me : Me : Me = =1 : 2 : 4 : 6. M.p. 216°. |
| Acettetramethylamido-benzene .. .. .. | NHAc : Me : Me : Me : Me = =1 : 2 : 3 : 4 : 6. M.p. 215°. |
| Acetpentamethylamido-benzene .. .. .. | NHAc : Me : Me : Me : Me : Me =1 : 2 : 3 : 4 : 6 : 6. M.p. 214 to 215°. |

That the $CH_3$ of the acetyl has an effect on the ortho- and para-position in the nucleus seems evident, as 1 : 2 : 4-formylxylid has the same melting-point as acetanilid (114°). Similarly, 1 : 3 : 5-acetxylid and 1 : 2 : 3 : 4 : 5-tetramethylformanilid have the same melting-point, viz., 144°.

The tetramethylformanilid can be imagined as built up of 1 : 3 : 5-formylxylid and 1 : 2 : 4-formylxylid.

| | |
|---|---|
| Melting-point of 1 : 2 : 4-formylxylid .. .. .. | 113·5° |
| „ 1 : 3 : 5 „ .. .. .. | 76·5 |
| | 190·0 |
| „ formanilid . .. .. .. | 46·0 |
| „ 1 : 2 : 4 : 5-tetramethylformanilid | 144·0 |

Formylmesidid and acetylxylid, NHAc:Me:Me = 1 : 2 : 6, have the same melting-point (176°). In this case the influence can only be exerted on one position (the para-), as both the ortho-positions are occupied.

Similarly, formylmesidid and 1 : 2 : 3-acetmetaxylid both melt at about 176°, and acetmesidid and 1 : 2 : 3-propionylxylid at about 216°.

As an example of numerical relations, taking formyl compounds, formanilid melts at 46°, pentamethylamidobenzene at 217°: now the melting-point of formanilid (46°) *plus* $2(34) = 114°$, which is the melting-point of formylmetaxylid, NHF : Me : Me = 1 : 2 : 4; again, the melting-point of formanilid *plus* $4(34) = 182°$, which is the melting-point of NHF : Me : Me : Me : Me = 1 : 2 : 3 : 4 : 6.

The formyl compounds of aniline, *p*-toluidine, 1 : 2 : 4-metaxylidine, and mesidine form a series:—

Aniline (46°); *p*-toluidine (52°); 1 : 2 : 4-xylidine (114°);
46 $= 46 + 6$ $46 + 6 + 62$
mesidine (176°), &c.
$= 46 + 6 + 2(62)$.

Similarly in the case of the corresponding acetyl compounds:—

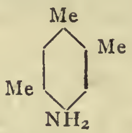
Aniline (114°); *p*-toluidine (147°); 1 : 3 : 4-xylidine (181°);
$= 46 + 2(34)$ $= 46 + 3(34)$ $46 + 4(34)$
mesidine (216°).
$46 + 5(34)$.

The different positions are not in all cases of equal value. Thus, pentamethylformanilid melts at 217°, and $46 + 5(34) = 216°$, which might indicate equality of the methyl groups, or rather of the positions in benzene. But when $CH_2$ is introduced into 1 : 2 : 4-xylidine to form mesidine, the melting-point rises 62°, so that the formula becomes—

$$\begin{aligned} 2 \times 34 &= 62° \\ 1 \times 62 &= 62 \\ 1 \times 46 &= 46 \\ \hline & 176 \end{aligned}$$

On introducing methyl into the meta-position, the melting-point rises to 182° in the case of 1-amido-2 : 3 : 4 : 6-tetramethylbenzene. The $CH_3$ groups *appear* again equivalent.

Again, taking away a methyl in the ortho-position leaves a pseudocumidine,—



,

melting at 121°, a drop of 62°.

These examples will suffice at present to show that definite relations between melting-points apparently do exist in the case of methylamidobenzenes. The authors have examined a number, and are gradually preparing other alkylamidobenzenes, containing ethyl, butyl, &c., and find also great regularities from which they hope to be able to state a general law. Many of the published data relating to melting-points undoubtedly require careful revision.

(To be continued).

## PHYSICAL SOCIETY.

*Ordinary Meeting, February 24th, 1893.*

Prof. A. W. Rücker, F.R.S., President, in the Chair.

Mr. Everett, jun., read a paper "*On a New and Handy Focometer*," by Prof. J. D. Everett, F.R.S., and exhibited the instrument described.

The focometer is constructed on the principle of the "Lazy tongs," and so arranged that the distance between the object and screen can be varied, whilst the lens is automatically kept midway between the two. This gives sharpest definition and the simplest calculation. The lazy tongs has eight cells formed by eighteen bars 13''×¾''×¼'', and is capable of being extended to about eight feet or closed up to about one foot. Brass pins about ¼ inch diameter and 1½ inches long project upward from each joint in the middle row, and serve as supports for clips carrying the lens, object, and screen. The instrument can be used for any lens whose focal length lies between 24 inches and 1 inch or less. To avoid error due to play in the joints, it is desirable to open or close the frame from both ends. The two chief disadvantages of the focometer are, first, its liability to flexure when much extended, and second, the rotation of the pins carrying the lens, &c., which necessitates re-setting of the clips after a large alteration of length has been made. Details respecting the most appropriate objects and screens, and practical hints about the working of the instrument are given in the paper. The question of what accuracy is obtainable is also briefly discussed.

Mr. A. Hilger thought the instrument was too flexible to be used for accurate work.

Mr. Blakesley said it would be a great improvement if the pins could be prevented from rotating. For this purpose it might be advantageous to slot the heads of the pins so as to fit on a straight bar. He also suggested that by using a plane mirror close behind the lens the light would be reflected back and the length of the focometer could be reduced by one half.

The President thought Prof. Everett never intended the instrument to compete, as regards accuracy, with the elaborate and expensive apparatus now used; but nevertheless, the focometer was a very valuable one, especially for students' work, and was particularly well adapted to impress upon them the facts relating to conjugate foci.

A paper on "*A Hydrodynamical Proof of the Equations of Motion of a Perforated Solid, with Applications to the Motion of a Fine Framework in Circulating Liquids*," by G. H. Bryan, M.A., was read by Dr. C. V. Burton.

The object of the paper, which is a mathematical one, is to show how the equations may be deduced directly from the pressure equation of hydrodynamics, without having recourse to the laborious method of "ignoration" of co-ordinates. The general hydrodynamical equations of a perforated solid are first considered, and the pressure equation expressed in terms of the velocity, potential, density, and the translational and rotational velocities of the liquid. The expressions for the mutual reaction between the solid and liquid are then reduced to the required form by repeated applications of Green's formula, and the results made use of for writing down the equations of motion of the solid. The author then shows that the motion of the solid can be determined in terms of Routh's modified Lagrangian function, and the form of that function found. The results are applied to determine the motion of a light framework of wires. When the framework has a single aperture it is shown that no force produces motion in its own direction, and no couple produces rotation about its own axis. In the case of a fine, massless, circular ring, the direction of whose axis is taken as the axis of $x$, a constant force along the axis of $y$ produces uniform rotation about the axis of $z$, and a constant couple about the axis of $y$ produces uniform translation along the axis of $z$. In conclusion, the author states that the results might be made to furnish mechanical explanations of certain physical phenomena.

Appended to the paper is a note by Dr. Burton relating to the proper measurement of the impulse of cyclic motion, and in a further note Mr. Bryan shows how the equations of motion may be deduced from Dr. Burton's suggestions.

The President said the author had done good service by attacking the difficult problem by elementary methods. He had also arrived at some very interesting conclusions, particularly the one showing that a perforated body moving through a liquid required no force to keep up the motion.

Dr. C. V. Burton made a communication "*On Plane and Spherical Sound-waves of Finite Amplitude.*"

The first part of the paper refers to plane-waves. This subject had been considered by Riemann, but Lord Rayleigh had criticised that part of Riemann's work where it is held that a state of motion is possible, in which the fluid is divided into two parts by a surface of discontinuity propagating itself with constant velocity, all the fluid on one side of the surface of discontinuity being in one uniform condition as to density and velocity, and on the other side a second uniform condition in the same respects. After quoting Lord Rayleigh's criticism, the author shows that the same objection applies when the velocity and density on either side of the surface may vary continuously in the direction of propagation, and the velocity of propagation of the surface of discontinuity is also allowed to vary. In each case the assumed motion violates the condition of energy, and can only exist under that special law of pressure for which progressive waves are of accurately permanent type. Enquiry is then made as to what becomes of waves of finite amplitude after discontinuity sets in (which condition must always occur with plane-waves), in the course of which it is pointed out that the front of an air disturbance, produced by a moving source which starts impulsively, travels faster than the source, even if the velocity of the source exceeds that of feeble sounds. A mechanical analogy is given which suggests that a dissipative production of heat takes place when discontinuity occurs.

In all cases Riemann had assumed that pressure is a function of density only, according to the isothermal or adiabatic law, and thus failed to take account of any heat which may be dissipatively produced.

The first part of Burton's paper is concluded by a short reference to Dr. Tumlirz's work on the subject, who infers that as soon as a discontinuity is formed it immediately disappears again, this effect being accompanied by a lengthening of the wave and a more rapid advance of the disturbance. In this way Dr. Tumlirz seeks to explain the increased velocity of very intense sounds. The author, however, considers that an increased velocity can only ensue when the motion has become discontinuous.

Part II. of the paper deals with spherical waves, and contains a mathematical investigation into the conditions under which the motion remains continuous or becomes discontinuous. The criterion is found in the finitude or infinitude of a certain integral. It is shown that if viscosity be neglected, then under any practically possible law of pressure the motion in spherical sound-waves always becomes discontinuous. For waves diverging in four dimensions some cases occur in which the motion remains continuous. The general question of spherical sound-waves of finite amplitude is then treated of, and the paper concludes with a method of finding the differential equation of an infinitesimal spherical disturbance which is superposed on a purely radial steady motion.

Prof. A. S. Herschel enquired whether the nature of the solution for plane-waves of finite amplitude was similar to that for ordinary wave-motion? In the latter case everything depended on the instantaneous impulses, for these alone determined the nature of the wave.

Referring to Mr. Bryan's paper, he (Prof. Herschel) asked if the author could apply his equations to centrifugal fans. A particular kind of double fan had recently been tested, and gave very anomalous results which had not yet been explained.

The President said Mr. Boys' experiments on flying-bullets might have some bearing on Dr. Burton's paper. If the conclusions there stated were correct, then the velocity of the air in front of a bullet should be greater than that of the bullet, even if the latter was travelling faster than ordinary sound-waves. He now asked Mr. Boys if his photographs gave any evidence of this.

Mr. Boys said the fact that the photographs showed disturbances in front of the bullet proved that the disturbance travelled faster. In one case, where a large bullet was moving at a velocity rather greater than that of ordinary sound in the medium, the front of the disturbance was about half an inch in advance of the bullet. In another instance, where the bullet was smaller and the velocity greater, the distance which the disturbance was in advance of the bullet was somewhat less. In all cases, even when the velocity of the bullet was four times that of sound, the character of the effects remained the same.

Dr. Burton replied to the points raised.

## INSTITUTE OF CHEMISTRY.

The Annual General Meeting of the Institute of Chemistry of Great Britain and Ireland was held on March 1st at 30, Bloomsbury Square, W.C., the premises recently acquired by the Institute.

The Report of Council and Balance Sheet for 1892 having been presented and approved, the Council and Officers for the ensuing year were elected, and the President, Dr. William A. Tilden, F.R.S., delivered an address in which, after referring to the satisfactory progress which had been made by the Institute during the past year, he proceeded to explain the new curriculum recently adopted by the Council for the training and examination of Associates, and the proposals which had been brought forward by the Censors with the object of regulating the professional conduct of Members of the Institute.

The numbers on the Register now are 826 members and 109 students, as compared with 823 members and 34 students at the date of the last Annual General Meeting.

## NOTICES OF BOOKS.

*Rules for the Spelling and Pronunciation of Chemical Terms.* Adopted by the American Association for the Advancement of Science in 1891.

These proposals, issued by the Bureau of Education, Washington, bear the signatures of Professors T. H. Norton, E. Hart, H. Carrington Bolton, and James Louis Howe, and recommend themselves to all English-speaking communities. In some cases, however, we venture to suggest that the proposed reforms might, without any risk of confusion, have been carried a little further.

The following general rules are laid down:—

1. The pronunciation is as much as possible in accord with the analogy of the English language.
2. Derivatives retain, as far as possible, the accent and pronunciation of the root-word.
3. Distinctly chemical compound words retain the accent and pronunciation of each portion.
4. Similarly sounding endings for dissimilar compounds are avoided.

A few alterations are made in the orthography of the names of the elements. Thus, for sulphur it is proposed to write sulfur, for which there is every reason, since the word is not of Greek origin. The names of the halogens are to drop the final *e*, and have the *i* in the last syllable pronounced short. Here we think a little further change would be desirable; we would suggest to cancel the last syllable of the names of the halogens altogether, and write simple chlore, fluor, &c. Then we would drop the needless *us* of phosphorus, and write phosphor. Manganese we would convert into mángan, which would make the word less liable to be confounded with magnesium.

The recommendation is given to abrogate arsenetted (or arseniuretted) hydrogen and the analogous antimony, sulfur, &c., compounds in favour of arsin, stibin, phosphin. Benzene and toluene are to be used in place of benzol and toluol. This change, however, has been in part anticipated. Not a few chemsts, whilst adopting benzene and toluene for the pure chemical individuals, retain benzol and toluol for the crude commercial products.

We have always used the terms "strength" or "standard" in place of titre, or, as it is written in America, "titer." We also use, as it is here recommended, "gramme," since "gram" is very apt to be confounded with grain. The termination "meter" is generally used in the names of pieces of apparatus, but in the names of measures we always write "metre." We are glad to see that the authors do not seek to spell barium as it is generally done on the Continent. The names glycerol, resorcinol, mannitol will not be very readily adopted in place of glycerin, resorcin, and mannite; nor are the pronunciations oxid, hydrid, &c., likely to find early favour. Perhaps the disagreeable custon of pronouncing oxygen and its paranyms as if written "ogsygen" does not prevail in America.

We wish some of our writers of elementary treatises on chemistry would take a leaf or two out of the book of the American chemists.

*On the Preservation of Solutions of Hydrogen Sulphide.* ("Sur la Conservation des Dissolutions de l'Acide Sulfhydrique.") By Professors A. E. Salazar and Q. Newman, of the Naval Military School of Chili. Translated from the Spanish by Manuel A. Délano. Member of the Scientific Society of Chili and of the Chemical Society of Paris. Paris: Imprimerie de la Cour d'Appel, 1892.

The authors draw from their experiments the following conclusions, which will now scarcely be called in question:—

The solution of $H_2S$ when made in pure water or in Lepage's mixture (water and glycerin) preserves the strength the less it is exposed to the action of air. For the preservation of the solution it is highly advantageous to dissolve the $H_2S$ in Lepage's mixture and not in water, as in the former the oxidation of the gas is slower than in pure water.

Light has little influence on the speed of oxidation, whether the $H_2S$ is dissolved in water or in the Lepage mixture. The oxidation is, however, more rapid in light than in darkness. Certain organic substances, added in small proportions to watery solutions of $H_2S$ modify the progress of oxidation, either by acceleration or retardation.

*Helbing's Pharmaceutical Record.* No. X., October, 1892. Reprinted January 25, 1893. London: 63, Queen Victoria Street, E.C.

*Notes on Eucalyptus Globulus and its Uses.* By Harry Benjafield, M.B. (Hobart). London, 1892.

These two pamphlets are written with a view to enlighten the public on the sanitary and medicinal properties of the true eucalyptus oil, obtained from the "Blue Gum Tree" of Tasmania, and to point out the difference of its composition and effects from those of preparations often substituted for it. Some of these oils are obtained from the "Peppermint Gum Tree" (*Eucalyptus amygdalina*), and others from the Mallee Scrub (*Eucalyptus dumosa*). The two latter are certainly derived from members of the great Eucalyptus tribe, but they are poor in eucalyptol and too irritating for use either internally or externally.

Where the *E. globulus* or true "fever tree" grows, fevers are very rare and low forms of animal and vegetable life dislike the locality.

Fruit trees experimentally mulched in autumn with leaves of *E. globulus* are found next season free from blights and fungi. If a little of this oil is injected into a rose tree covered with aphides, the vermin all disappear in a few days. It is therefore exceedingly unfortunate that the products of *E. amygdalina* and *E. Dumosa*, relatively poor in eucalyptol, are commonly sold under the general, though misleading name of eucalyptus oil.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 8, February 20, 1893.

At the meeting of the Academy for nominating a correspondent for the section of chemistry, vice the late Prof. Stas, Prof. Kekulé was elected. He obtained forty-seven votes as against two given to Prof. Mendeleeff, and one each given to Prof. Cannizzaro and Sir H. Roscoe.

**Preparation of Uranium at a High Temperature.**—Henri Moissan.—This paper will be inserted in full.

**Rapid Preparation of Chrome and Manganese at High Temperatures.**—Henri Moissan.—This paper also will appear *in extenso*.

**On Stereochemistry.**—C. Friedel.—A reply to M. Colson's paper (*Comptes Rendus*, cxvi., p. 994). The author contends that M. Colson does not attack stereochemistry as recognised by its upholders, but certain inexact ideas of his own, and that he has failed to understand the abbreviated formula of van 't Hoff.

**Diazoamidobenzene and Paradiazoamidotoluene Benzoates, and Metanitrobenzoates.**—A. Haller and A. Guyot.—The authors have employed the method of Knœvenagel (*Berichte*, xxiii., p. 2957) for obtaining solid diazobenzene chloride, sulphate, and nitrate. This method consists in treating an alcoholic solution of a mixture of amine and of organic acid with amyl nitrite and isolating the precipitation. In this manner they have obtained diazoamidobenzene benzoate, diazoamidobenzene metanitrobenzoate, paradiazoamidotoluene benzoate, and paradiazoamidotoluene metanitrobenzoate. Attempts to obtain diazoamidobenzene acetate, formiate, and orthotoluate, have not proved successful, the result being always pure, crystalline diazoamidobenzene. The authors have also tried the action of amyl nitrite upon a mixture of ethyl cyanacetate or acetylacetate and of paratoluidine. In both cases the sole product was diazoamidotoluene.

**New System of Atomic Weights founded in part on the Direct Determination of the Molecular Weights.**—A. Leduc.—The system of atomic weights generally adopted includes among its fundamental determinations that of the composition of potassium chlorate, which gives room for doubt. The author has recently shown that the atomic weight of oxygen is 15·88, the density of this gas with reference to air being 1·10503, and that of nitrogen 0·97203. He has more recently established that the molecular volume of carbon monoxide, with reference to oxygen under normal conditions, is close upon 1·0001. Hence we are led to admit that nitrogen and carbon monoxide, by reason of the proximity of their critical points, have the same molecular volume within about 1 10,000th part. Hence the atomic weight of nitrogen is $15{\cdot}88 \times \frac{0{\cdot}97203}{1{\cdot}10503} \times 1{\cdot}10001 = 13{\cdot}97$. The determinations of Stas lead to the value 13·94. According to the author's experiments $NO_3 = 61{\cdot}61$, and consequently $Ag = 107{\cdot}17$. He finds for Cl the value 35·21, for Br 79·39, and for I 125·96. He finds for carbon the atomic weight 11·916.

**Decomposition of Alkaline Aluminates by Carbonic Acid.**—A. Ditte.—A current of carbonic acid passed into a solution of an alkaline aluminate containing an excess of alkali will give different results according to the magnitude of this excess, so that we may have or fail to have crystals of hydrated alumina. If the liquid is rich in alumina and poor in alkali, crystals are quickly formed. With a solution rich in alumina and poor in aluminate we may obtain merely a precipitate of the double carbonate.

**Mixtures of Ether and Water.**—L. Marchis.—The vapour tension of a mixture of ether and water is independent of the composition of the liquid, provided that we have a solution of water in the ether or a mixture formed of two strata.

**Formation-Heat of Arragonite.**—H. Le Chatelier.—The author finds the heat of the transformation of arragonite into calcite −0·3 cal.

**Ammoniacal Fermentation of Soil.**—A. Muntz and H. Coudon.—The formation of ammonia in the soil which is observed, especially after the use of organic manures, is due to the intervention of lower organisms and not to a chemical action. The organisms which produce this transformation appear to be numerous.

**Composition of the Salts employed as a Condiment by the Population near the Oubangui.**—J. Dybowski and Demoussy.—The tribes concerned use as a condiment to their food saline matter, composed of potassium chloride, sulphate, and carbonate, and containing no sodium. It is obtained by lixiviating the ashes of certain plants, ferns, aroids, gramineæ, and polygonaceæ. It results that potassium chloride and sulphate may be ingested with impunity in considerable quantity.

**Oxyhæmatine, Reduced Hæmatine, and Hemochromogen.**—H. Bertin-Sans and J. Moitessier.—The authors show that by the direct action of reducing agents upon alkaline (not ammoniacal) solutions of pure oxyhæmatine there is formed not hæmochromogen, but a compound with a special spectrum, which they propose to name reduced hæmatine. This compound yields secondarily hæmochromogen, by the action of ammonia, of amines, and of albumenoids.

## *Bulletin de la Société Chimique de Paris.*

Series 3, Vols. ix. and x., No. 1, January 5, 1893.

**Determination of Extract left on the Evaporation of Wine.**—J. A. Müller.—The author determines the weight of the dry extract left on the evaporation of a wine at 100°, and the extract left on evaporation in a dry vacuum.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Testing for Cotton in Woollen Goods.**—What is the chemical used for testing woollen material to see if cotton is mixed with it? The test that I have seen takes away every partial wool and leaves cotton warp behind —F.S.C.

**Aluminum Sulphide.**—Will the correspondent who wrote for information regarding aluminum sulphide some time ago from Hotel Metropole, Brighton, write again, as that address is unknown?—H. N. Warren, 18, Albion Street, Liverpool.

## MEETINGS FOR THE WEEK.

Monday, 13th.—Medical, 8.30.
—— Society of Arts, 5. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
Tuesday, 14th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Physical and Psychical Neurology," by Prof. Victor Horsley, F.R.S.
—— Photographic, 8.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 15th.—Society of Arts, 8. "Technical Education—its Progress and Prospects," by Sir Philip Magnus.
—— Meteorological, 7.
—— Microscopical, 8.
Thursday, 16th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Great Revival—A Study in Mediæval History," by the Rev. Augustus Jessopp, D.D.
—— Chemical, 8. "Limits of Accuracy of Gold-Bullion Assay and the Losses of Gold Incidental to it," by T. K. Rose. "Boiling-point of Liquid Nitrous Oxide at Atmospheric Pressure, and on the Melting-point of Solid Nitrous Oxide," by W. Ramsay, F.R.S., and John Shields, Ph.D. "Isomerism of Aliphatic Aldoximes," by W. R. Dunstan and T. Dymond. "Formic Aldoxime," by W. R. Dunstan "Properties of α-Benzaldoxime," by W. R. Dunstan and M. C. Luxmore.
Friday, 17th.—Royal Institution, 9 "Ancient Egyptian Pigments," by W. J. Russell, F.R.S.
—— Quekett Club, 8.
Saturday, 18th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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## FLETCHER'S THERMO-HYDROMETER.

It is scarcely necessary to insist upon the vital importance of noting the temperature of a liquid when determining its specific gravity Hitherto it has been necessary to employ separate instruments for the two observations, such combinations as were available being clumsy, slow, and untrustworthy. In FLETCHER'S THERMO-HYDROMETER the bulb of the Thermometer is BLOWN IN ONE PIECE WITH THE BULB OF THE HYDROMETER, and comes into direct contact with the liquid to be tested, thus ensuring the utmost sensitiveness. The Thermometer and Hydrometer scales being in juxtaposition on the same stem, A READING OF EACH CAN BE TAKEN SIMULTANEOUSLY.

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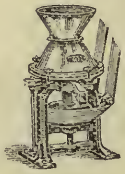

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1738.

## ESTIMATION OF UREA.

By WALTER COLQUHOUN, M.A.

Dissatisfied with the inaccuracy and the labour involved in the methods of estimating urea for clinical purposes at present in vogue, I was led to devise the arrangement which I describe.

My apparatus consists of a burette, B, graduated from the stopcock, S, S, to show tenths of a c.c., and attached by a piece of indiarubber tubing to a tube, T, carrying two side tubes, as shown in the drawing, and widened at A to hold about 15 c.c. between the lower side tube and the stopcock $S_2$. Below the stopcock $S_2$ the tube is widened to a bulb, C, which holds about 6 c.c., and a stopcock, $S_3$, is placed below the bulb. The side tubes are connected by indiarubber tubing with reservoir $R_1$ and $R_2$, of which $R_1$ holds water and $R_2$ sodium hypobromite or hypochlorite. As the reservoir $R_2$ is not moved, the indiarubber tubing may, in its case, be replaced by glass tubing and a stopcock. Clips are placed on the indiarubber tubing to control the flow of the fluid in the reservoirs, and the apparatus is mounted on a suitable stand with rests for the reservoirs. It is worked as follows:—

The stopcock $S_2$ is withdrawn, and the stopcock $S_3$ having been closed, a measured quantity of urine is introduced into the bulb C by means of a pipette curved at the delivery end, so that it may be inserted into the hole leading from the stopcock $S_2$ to the bulb. The stopcock $S_2$ is then replaced, and water is run in from the reservoir $R_1$ until it rises above the hole in the stopcock, which is then shut. Sodium hypobromite is then run in to the desired amount from the reservoir $R_2$, and water is then run in from $R_1$ to fill the burette, the stopcock $S_1$ being then closed.

On now opening $S_2$ nitrogen is evolved, and atmospheric pressure may be maintained by holding $R_1$ at the proper level, taking care that the clip on the tube leading to $R_1$ is open. After reading the amount of nitrogen $S_1$ is opened, and then $S_2$, and the apparatus rinsed out with water from $R_1$, when it is ready for another estimation.

To do away with repeated corrections for temperature, pressure, and tension of aqueous vapour, I introduce by means of my pipette, which is graduated on the stem and can measure to 1-100th of a c.c., the amounts of urine given in the following table, which are calculated so that the quantity given under a certain temperature and pressure evolves as many c.c. of nitrogen as the urine contains grms. of urea per litre, or weighed grains per thousand measured grains.

The table is given for rises in pressure of 10 m.m. and in temperature of 5° F., but the differences are so constant that it is easy to interpolate for intervening temperatures and pressures.

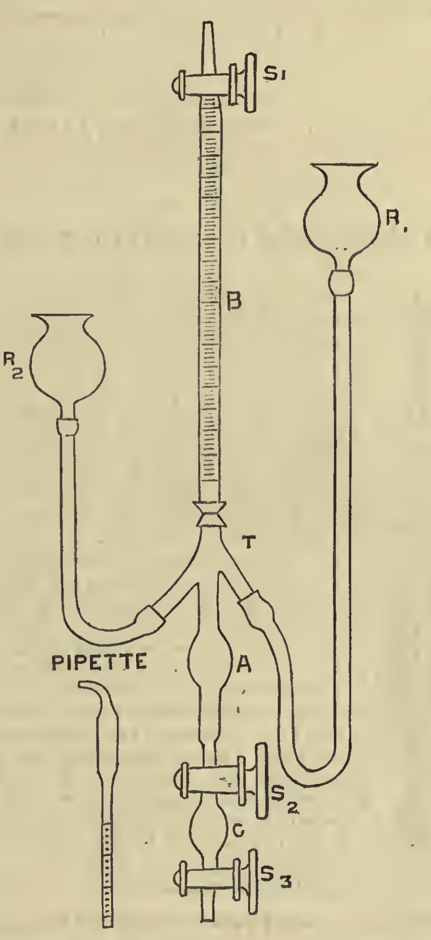
My apparatus is an improved form of Russell and West's, but even those who prefer to use Apjohn's apparatus, or Dupré's modification of it, would find it an advantage to use the measurements given in the above table, or preferably to use, as I did in my experiments, double the quantities given, so that every 2 c.c. of nitrogen count one part of urea per thousand. My experiments were made with an apparatus double the size of that described, and the results may be briefly stated as follows:—

1. Using sodium hypobromite prepared according to Russell and West's directions, and the quantities of fluid given in the table, which is calculated for an evolution of 92 per cent of N, the results equal in accuracy those of any other chemical analysis under ordinary conditions.

2. The water and hypobromite used should be allowed to gain the temperature of the laboratory before using, and on no account should heat be applied unless time be afterwards given for the apparatus to cool down to the surrounding temperature. It is quicker and more accurate to let the action take place in the cold.

3. There is no tendency to re-absorption of the N, as is seen from the details of my experiments, in most of which readings were taken at the end of twenty-four hours.

4. The hypobromite should not be added too quickly. In the apparatus which I found to work best, the hole in the stopcock $S_2$ is one-quarter inch in diameter.



I have made about thirty estimations with my apparatus with solutions of urea of known strength at temperatures varying from 50° F. to 65° F. In each case I took double the amount of fluid given in the table, and I give details of a few estimations to show my method of working.

*2 per cent Solution.*

I.—Temperature 55° F.; Pressure 29·7 in.;
5·46 c.c. taken.
N evolved at end of 20 minutes 40 c.c. = 2 per cent urea.
" " " 24 hours 40·3 " = 2·015 " "

1·8 *per cent Solution.*

II.—Temperature 50° F.; Pressure 29·7 in.;
5·53 c.c. taken.
N evolved at end of 10 minutes 35·8 c.c. = 1·79 p.c. urea.
" " " 1 hour 36 " = 1·8 " "
" " " 24 hours 36 " = 1·8 " "

*Pressures.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Inches .. .. .. .. .. | 28·35 | 28·74 | 29·14 | 29·53 | 29·92 | 30·31 | 30·71 | 31·10 | 31·49 |
| Millimetres .. .. .. .. | 720 | 730 | 740 | 750 | 760 | 770 | 780 | 790 | 800 |
| 40° F. .. .. .. .. .. | 2·700 | 2·738 | 2·776 | 2·814 | 2·852 | 2·889 | 2·927 | 2·965 | 3·003 |
| 45° F. .. .. .. .. .. | 2·669 | 2·706 | 2·743 | 2·781 | 2·818 | 2·856 | 2·893 | 2·930 | 2·968 |
| 50° F. .. .. .. .. .. | 2·636 | 2·673 | 2·710 | 2·747 | 2·784 | 2·822 | 2·859 | 2·896 | 2·933 |
| 55° F. .. .. .. .. .. | 2·604 | 2·640 | 2·677 | 2·714 | 2·751 | 2·788 | 2·824 | 2·861 | 2·898 |
| 60° F. .. .. .. .. .. | 2·571 | 2·607 | 2·644 | 2·680 | 2·716 | 2·753 | 2·789 | 2·826 | 2·862 |
| 65° F. .. .. .. .. .. | 2·537 | 2·573 | 2·609 | 2·646 | 2·681 | 2·717 | 2·753 | 2·790 | 2·826 |
| 70° F. .. .. .. .. .. | 2·503 | 2·538 | 2·574 | 2·610 | 2·646 | 2·681 | 2·717 | 2·753 | 2·788 |
| 75° F. .. .. .. .. .. | 2·468 | 2·503 | 2·538 | 2·574 | 2·609 | 2·644 | 2·680 | 2·715 | 2·750 |
| 80° F. .. .. .. .. .. | 2·431 | 2·466 | 2·501 | 2·536 | 2·571 | 2·606 | 2·641 | 2·676 | 2·711 |

*2 per cent Solution.*

III.—Temperature 60° F.; Pressure 29·5 in.;
5·36 c.c. taken.

N evolved at end of 20 minutes 39·8 c.c. = 1·99 p.c. urea.
„ „ „ 24 hours 39·95 c.c. = 1·997 „ „

*1 per cent Solution.*

IV.—Temperature 55° F.; Pressure 29·2 in.;
5·37 c.c. taken.

N evolved at end of 20 minutes 20 c.c. = 1 p.c. urea.
„ „ „ 24 hours 20·1 „ = 1·005 „ „

My maximum deviation from accuracy was an excess of four-tenths of a c.c. on 36 c.c. of nitrogen, which gives 1·82 per cent urea instead of 1·8 per cent, and it would appear since my deviations were nearly all errors of excess, that under my conditions the urea gives up on long standing from 92 to 92·7 per cent of nitrogen. I preferred to calculate my table for an evolution of 92 per cent, because if the tube be tapped to dislodge any bubbles of gas which may adhere to the sides and to start small bubbles to the surface, the reading at the end of twenty minutes is almost accurate.

My maximum error was slight in comparison with the errors which may arise owing to neglect of corrections for temperature, pressure, and tension of aqueous vapour. Thus, if at the extreme temperatures and pressures of the table the number of c.c. given for 60° F. and 760 m.m. were taken, the error would amount to 0·2 per cent, or 0·23 per cent of urea on a 2 per cent solution.

I think I may claim to have reduced manipulation and calculation to a minimum with my arrangement, which at the same time gives perfectly reliable results. The measurement and introduction of the urine, the opening and shutting of stopcocks, and a reading at the end of twenty minutes is all that is demanded from the experimenter. Another opening of stopcocks washes out the apparatus, which is then ready for another analysis.

Mr. Otto Muller, 175A, West George Street, Glasgow, has been authorised to supply the apparatus.

67, Gibson Street, Hillhead, Glasgow.

## ON THE PREPARATION OF URANIUM AT A HIGH TEMPERATURE.

By HENRI MOISSAN.

Of late years metallurgy has utilised powerful currents for producing electrolyses. The new preparations of magnesium and aluminium are instances, but we consider that the heat produced by the electric arc may also be especially utilised when it is required to reduce with carbon certain oxides hitherto regarded as not capable of reduction.

Thus the use of the electric furnace enables us quickly to prepare the refractory metals, which hitherto could be obtained only with difficulty, or not at all.

It is merely needful to place in the cavity of a furnace of lime a certain quantity of magnesium, which is absolutely stable at the highest temperatures of the arc, and to arrange above it a crucible of retort-coke containing the mixture of carbon and oxide to be reduced.

If the metal is volatile, we cause the furnace to be traversed by a current of hydrogen and the metallic vapours are condensed in a refrigerated receiver. In this manner we prepare calcium, barium, and strontium. If the metal is not appreciably volatile, it remains at the bottom of the crucible in the form of an ingot. This is the case with uranium, the preparation of which we are about to describe.

Metallic uranium had been obtained by Peligot in very small quantities and with great difficulty by reducing uranium oxide with an alkaline metal. At ordinary temperatures the uranium oxides are not reducible by carbon. It is not the same, as I have already intimated, at the high temperatures which we can apply in the electric furnace.

To obtain this metal we ignite, in a porcelain capsule, uranium nitrate, which may be prepared in a state of great purity. There remains a reddish mixture of uranium sesquioxide and of the green oxide $U_3O_4$. We add to this mixture a slight excess of charcoal in powder, and the whole is strongly compressed into a coke crucible. On submitting this mixture, in the electric furnace, to the action of the arc produced by a current of 450 ampères and 60 volts the reduction is completed in a few moments. After cooling, we extract from the crucible a metallic ingot of a brilliant fracture and of great hardness, which if thrown upon porcelain, or if its fragments are agitated in a glass bottle gives brilliant sparks from the combustion of traces of the substancs. There occurs—though with far greater lustre—a phenomenon analogous to the combustion of particles of iron which take fire by simple friction in the air.

The yield of uranium by this process conducted in the electric furnace is very great. An experiment lasting twelve minutes yielded a regulus of from 200 to 220 grms. The 600 grms. which I have the honour of presenting to the Academy have been prepared in these operations, each reduction requiring only about ten minutes.

This sample does not consist of pure uranium.* It is a true cast-metal, and its proportion of carbon varies with the predominance, whether of the oxide or of the coke in the mixture.

A qualitative examination showed that merely uranium and carbon were present.

Determinations of different specimens of this uranium carbide gave the following results:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| U .. .. | 86·25 | 89·46 | 89·10 | 95·70 |
| C .. .. | 13·50 | 11·03 | 10·24 | 5·02 |

---

* A rather large number of metals have never been obtained in a state of perfect purity: some contain carbon, silicon, or the alkaline metals. We know now that a very small quantity of these impurities may modify the physical and even the chemical properties of these elementary bodies. To us it seems important to determine with care the state of purity of the metals obtained by means of the electric furnace.

We add that these uranium carbides slowly decompose water at the ordinary temperature—a property to which we shall have occasion to revert—and that their melting point is much higher than that of platinum.

In fine, we have obtained a true cast-uranium at a high temperature by the direct reduction of the oxides of uranium by coke. In a future research we shall give the characteristic properties of this compound, and indicate how it may be refined and what are the properties of the pure metal.—*Comptes Rendus*, cxvi., No. 8.

## THE DETECTION AND DETERMINATION OF ARSENIC.*

By JOH. THIELE.

### 1. *Hypophosphorous Acid as a Reagent for Arsenic.*

It has already been observed that arsenic is precipitated in a metallic state on prolonged ebullition with hypophosphorous acid. According to Thiele this reduction may be effected without evaporative boiling in a hydrochloric solution and with hypophosphorous acid which is not highly concentrated. By means of this reaction arsenic may be rapidly and conveniently detected even in presence of antimony and tin.

For this purpose the solution containing arsenious or arsenic acid is strongly acidified with hydrochloric acid, and to every 10 c.c. of the liquid there is added at least 1 grm. commercial sodium hypophosphite. On heating for some time on the water-bath the arsenic falls as a brown or blackish brown powder. If the liquid is very dilute it must be heated for a considerable time up to thirty minutes. If the amount of arsenic present is very small, the precipitate does not subside, but the liquid takes a brownish colour, which is especially visible if it is regarded obliquely downwards. In a sulphuric solution and in the absence of a hydracid the reduction takes place either not at all or very imperfectly. Hence it seems not to be an oxygen compound of arsenic but arsenic chloride, which is reduced by hypophosphorous acid. According to Thiele, arsenic iodide is still more easily reduced than arsenic chloride, so that an addition of potassium iodide or hydriodic acid expedites the reaction and renders it more sensitive. Whilst in the absence of potassium iodide 0·05 grm. arsenious acid is necessary to occasion a brownish reflexion in from 5 to 10 c.c. of liquid, 0·025 grm. is sufficient on the addition of a small crystal of potassium iodide.

Saving the precious metals which are likewise reduced by hypophosphorous acid, the presence of copper only absolutely interferes with the reaction, as this metal is precipitated even from a very dilute solution of the same colour as arsenic. Arsenic and bismuth are precipitated only from very concentrated solutions, but the precipitation is incomplete whether with or without the addition of potassium iodide. The precipitates given by these metals are distinguished from that of arsenic by their black colour. If the colour of the precipitate renders it probable that one of the two metals is present, the deposit is placed upon a small filter, and without washing it is taken up with a few drops of bromine in hydrochloric acid. From this solution, on repeating the reduction, the arsenic alone is deposited with its characteristic colour. In presence of antimony and bismuth—the latter especially—the addition of potassium iodide may be advantageously omitted, since the intense yellow colour occasioned by the iodides of these metals interferes with the sensitiveness of the reaction. From the same reason in the presence of large proportions of iron the air must be excluded as far as possible from the reduced and decolourised liquid to prevent the formation of iron chloride.

For the quantitative determination of iron and its separation from antimony and tin, the process with sodium hypophosphite seems unsuitable, as the arsenical deposit is extremely readily oxidised and cannot be washed.

### 2. *On the Use of the Marsh Apparatus for Detecting Arsenic in Presence of Antimony.*

By occasion of an investigation of Tookey's process for the separation of antimony and tin, Thiele inquired whether during the precipitation of antimony by iron any loss occurs by the formation of antimony hydride, and he found that in accordance with earlier observations, solutions of antimony do not evolve stibine with iron and hydrochloric acid and iron. As arsenic hydride is evolved from arsenical compounds under similar conditions, this process would afford a means of recognising arsenic in presence of antimony. But for this purpose only iron can be suitable which is free or approximately free from sulphur, since the presence of sulphur may entirely prevent the recognition of small quantities of iron in consequence of the formation of hydrogen sulphide. The production of such iron was connected with unexpected difficulties. The author succeeded only after a number of experiments in obtaining an iron electrolytically which contained merely a minimum of sulphur.

For its preparation 200 grms. commercial ferrous chloride, free from water of crystallisation, was dissolved in 500 c.c. of water, digested persistently in heat with the purest possible iron from former operations in order to remove any electro-negative metals which might be present, and mixed with barium chloride in order to remove sulphuric acid.

The filtrate, after the addition of 25 c.c. of glacial acetic acid, was submitted to electrolysis by means of a Bunsen element. The negative electrode consisted of a sheet of platinum, and the positive electrode of a plate of the purest iron procurable. As the impurities of the latter are deposited at the bottom in the form of a black mud, the piece of platinum must terminate 2 c.m. above the bottom of the vessel, so that it may not come in contact with the latter.

In order to prevent the oxidation of the solution of ferrous chloride by the oxygen of the air, the decomposition cell was placed in a glass cup containing a little water and covered with a glass ball. The polar wires are carried up through the water in the decomposing cell. They do not require insulation on account of the low conductivity of pure water. With one Bunsen element and a polar surface of 100 square c.m., 2 grms. iron may be deposited hourly. The solution of chloride may be repeatedly used after the addition of some acetic acid.

The iron obtained in this manner must be at once rinsed with water, alcohol, and ether, and dried *in vacuo* over sulphuric acid. If this iron is used in a Marsh apparatus with dilute hydrochloric acid as developing liquid, it yielded no mirror of arsenic or antimony, whether alone or after addition of a considerable quantity of pure antimony chloride. The gas was passed through a layer of wadding 10 c.m. in length. After an addition of arsenic or arsenious acid there appeared at once a copious formation of arsine.

In a quantitative experiment the appparatus was charged with iron and hydrochloric acid, and a weighed quantity (0·16 grm.) of arsenious acid. Hereby, however, only 10 per cent of the existing arsenic was converted into arsine and recovered as arsine, whilst copious black flocks of arsenic remained behind in the developing vessel.

An experiment undertaken in the same manner with non-platinised zinc and hydrochloric acid gave about 94 per cent of the arsenic present as arsine. Here also arsenic remained in the gas generator after the completion of the experiment.

This difference in the behaviour of zinc and iron,

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* From the *Zeit. Anal. Chemi*

according to the further experiments by the author, is to be explained by the circumstance that iron evolves arsine less readily from the precipitated arsenic than does zinc. Hence the detection of arsenic with iron is much less sensitive and succeeds only down to 0·1 or 0·15 m.grm.

The sensitiveness of the reaction is considerably increased if antimony chloride is simultaneously introduced into the apparatus. It is then easily practicable to detect 0·015 m.grm. arsenic in whatever state of oxidation it may be present.

The reaction certainly requires a longer time than the use of zinc, about two hours. Lest the development of hydrogen should become too violent, the solution of antimony (2 to 3 c.c. of a concentrated solution of oxychloride in hydrochloric acid of specific gravity 1·124), are added gradually.

Tin ranks intermediately in its behaviour between zinc and iron, as it is only able to evolve stibine in traces.

(To be continued).

## SOLID AIR.

Professor Dewar communicated to the Royal Society at its meeting on Thursday, March 9, a most interesting development of his experiments upon air at very low temperatures. Our readers are already familiar with the fact that he has liquefied air at ordinary atmospheric pressure. He has now succeeded in freezing it into a clear, transparent solid. The precise nature of this solid is at present doubtful, and can be settled only by further research. It may be a jelly of solid nitrogen containing liquid oxygen, much as calves' foot jelly contains water diffused in solid gelatin. Or it may be a true ice of liquid air, in which both oxygen and nitrogen exist in the solid form. The doubt arises from the fact that Prof. Dewar has not been able by his utmost efforts to solidify pure oxygen, which, unlike other gases, resists the cold produced by its own evaporation under the air pump. Nitrogen, on the other hand, can be frozen with comparative ease. It has already been proved that in the evaporation of liquid air nitrogen boils off first. Consequently the liquid is continually becoming richer in that constituent which has hitherto resisted solidification. It thus becomes a question whether the cold produced is sufficiently great to solidify oxygen, or whether its mixture with nitrogen raises its freezing-point, or whether it is not really frozen at all, but merely entangled among the particles of solid nitrogen, like the rose-water in cold cream. The result, whatever may be its precise nature, has been attained by use of the most powerful appliances at command—a double set of the vacuum screens already described in our columns, combined with two powerful air pumps. Upon either view of its constitution, the new solid is in the highest degree interesting and hopeful.—*Times.*

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 116).

### *Our First Series of Syntheses.*

In it our original intention was to set up as close an imitation of Dumas's apparatus as we might be able to construct, and, by means of it, to carry out a few syntheses exactly in his style in order to fortify our position as critics of his work, and, in the most direct manner possible, to decide the important question whether he really had, as we suspected, forgotten to reduce his water-weights to the vacuum. But we soon came to give up this idea, for this reason amongst others, that we had not a high-class air-pump at our disposal, and *without such an instrument we thought at the time* we should not be able to weigh our oxide of copper and metallic copper *in vacuo*, as he did. We had to modify Dumas's method so as to bring it within the range of our resources, and this being so, we thought we might as well try and improve upon it by utilising our method for the production of absolutely oxygen (*i.e.*, $O_2$) free hydrogen, and by working on a smaller scale. We were, and to this day are, convinced that Dumas positively lost precision by working with such extraordinarily large quantities of oxide of copper, that he had to execute his final weighings after having become exhausted by "from fifteen to twenty hours" of continuous work. We have no doubt in our own minds that our results are at least as close approximations to the truth as his, although we worked on such a small scale that we were able to carry out all our weighings with a balance of only "100 grms. carrying power" (the actual charge, it is true, sometimes rose to 120—130 grms.), and were able to complete a synthesis without working longer than from about nine in the morning to five to six in the evening. Dumas tells us that his nineteen published experiments correspond to no less than forty to fifty such experiments actually made, which means about one failure for every two attempts. Of the thirteen actual syntheses which we made, only *one* was a breakdown, and *one* other had to be rejected on account of unobserved blunders.

For the production of the necessary continuous supplies of hydrogen we used two "Kipps," which were coupled together by means of one of those admirable two-way cock arrangements of Messrs. Greiner and Friedrichs, so that we were able to use either one or the other, and, supposing one to be exhausted, to re-charge it while the other was working. Let us add at once that we never had occasion to do this. In a few of the first trials (with small quantities of oxide of copper) we used 10 per cent hydrochloric acid for liberating the gas, but all the later experiments were made with 20 per cent sulphuric acid. For the purification of the gas we used at first to pass it successfully through, (1) cotton-wool; (2) a U-tube charged with vitrioled pumice; (3) a combustion tube 370 m.m. long and 15 m.m. wide inside, containing as thick a closely-wound spiral of fine copper gauze as it would hold, and drawn out at each end to avoid the use of corks. This tube was kept at a red heat during the progress of an experiment, and served to eliminate the antimony, arsenic, and sulphur which the gas contained, besides converting the oxygen of the unavoidable trace of air into water, which latter was caught in a U-tube charged with vitrioled pumice attached to the outlet. The principal impurity in our zinc was antimony; we therefore, in our later experiments, purified our gas by sending it from the "Kipp" direct into a large tower (210 m.m. high and 35 m.m. wide), filled with fragments of caustic soda, which converted almost the whole of the antimoniuretted hydrogen into a black deposit of SbOH. From the soda-tower the gas passed into the tube containing red-hot copper.

*The Oxide of Copper* was prepared from chemically pure copper foil by cutting it up, placing it in a Berlin basin, and, in it, heating it in a muffle for a day or two. The muffle was new, and, during the progress of the research was never used for any other work. The only impurity which the oxide could have contained is sulphur (from the gas-flames); we therefore tested about 10 grms. of it by treating it with pure fuming nitric acid, &c., and searching for sulphuric acid by means of chloride of barium. From the whole of the 10 grms. of oxide used only a barely visible trace of a precipitate was obtained, which amounted to no more than the one seen in the "blank" which accompanied the experiment proper. Oxide of copper produced in the way described never contains the full proportion of oxygen demanded by the formula CuO, but this does not matter; over the oxide

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* *Proceedings of the Philosophical Society of Glasgow.*

produced by heating the nitrate it offers the inestimable advantage of not being hygroscopic. When we had used up the first supply of oxide, the metal obtained from it was re-oxidised in the muffle, which took far less time than the oxidation of the original compact metal.

Our apparatus is represented in the Figs. 3.1, 3.2, 4 and 5.

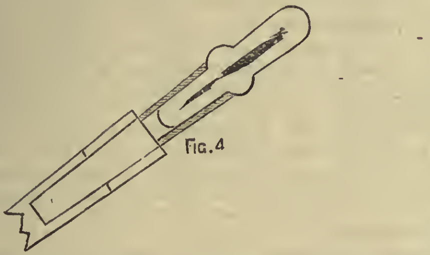

Fig. 4

The reduction-tube, L, was made out of a piece of wide combustion-tubing. When used, it was heated in a magnesia-bath by means of a set of Bunsens, a roof-shaped chimney made of asbestos pasteboard serving to reflect down the heat on the top part of the tube. In the original apparatus this tube was connected with the outlet of the preceding vitriol-tube by means of an india-rubber stopper, which, as we may state, was taken out before the apparatus went to the balance. But we subsequently discarded the stopper and substituted for it the arrangement shown more clearly in Fig. 5, for the explanation of which it suffices to state that the joints at K and *k'* were made tight by means of strips of warm non-vulcanised sheet india-rubber wound round and secured by wire ligatures on both sides.

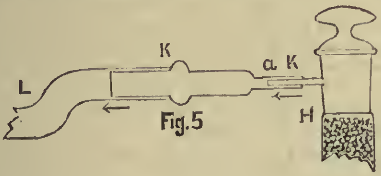

Fig. 5

The water-receptacle, P, was made out of a fractionating flask. Fig. 3.2 shows its construction and mode of connection with the reduction-tube. The tube, *d*, is fixed in its place by means of a cork, *g*, which terminates a little below the edge of the neck of the flask so as to form a cup, which is filled completely with sealing-wax so as to avoid contact between air and cork. The outlet of the reduction-tube O, in Fig. 3.1, and, *a*, in Fig. 3.2, projects into the tube *d*, the joint at *b* being made tight by means of a wired-on band of black sheet india-rubber, as in the case of the improved form of the reduction-tube entrance. After a few experiments had been made with the apparatus as described, we found that, sometimes, a sublimate of water settled down in the annular space between *d* and *a*. To prevent this inconvenience, we provided the arrangement represented in Fig. 6. H is the last drying-tube preceding the reduction-tube. The original intention was to close the stopcock, *b*, whenever a sublimate of water shows itself between *a* and *d*, and let the gas go through the side-tube, *c d e f*. But we subsequently found it easy to adjust the cocks *b* and *d*, so that a small portion of the hydrogen went constantly through the side-tube and swept down any steam present within that annular space that might otherwise have condensed into a sublimate of water.

The weighings were effected by means of that very excellent Oertling's "14-inch," which one of us described in the *Zeit. fur Instrumentenkunde* some years ago, and a set of iridio-platinum weights from Johnson, Matthey, and Co., which were adjusted by Oertling, and subsequently readjusted by one of us (W.D.), with the co-operation of his then assistant, Mr. Barbour. To reduce the uncertainties of the weighings to a minimum, the several portions of the apparatus were tared with somewhat lighter similar apparatus of as nearly as possible the same displacement, so that the weight standards lying on the pan represented little more than the net weight to be determined.

In the execution of the syntheses the exact *modus operandi* was not always exactly the same. Little improvements were introduced as our experience expanded, but there would be no use in here giving the history of our apprenticeship; it suffices to describe the *modus operandi* in its latest form, which, indeed, was employed in all the actual syntheses intended for the calculation of the value $H_2 : O$.

The first step in each case was to start the hydrogen and let it go through the purifiers, the copper tube being meanwhile kept at the ordinary temperature. The reduction-tube was then charged with a suitable quantity of oxide of copper, and prepared for the balance by heating the oxide in a current of vitriol-dried air, until every trace of moisture was sure to be expelled. The tube was then allowed to cool in dry air, closed at both ends, and next kept immersed in a water-bath of the temperature of the balance room, beside the tare tube, until both could be assumed to have acquired that temperature. The two portions of the apparatus were then taken out of the bath, wiped dry with a towel, and suspended at the balance, the working tube at the left end and the tare tube at the right, a special tare equal in weight to the stopper and cap on the working tube being placed in the right pan. After some time the working tube was opened for a second to bring its atmosphere to the pressure of the air outside, and equilibrium established by means of weights. Some ten minutes later the weights were re-adjusted, and this operation was repeated until the state of equilibrium had become permanent, which always was the case after a short time—thanks chiefly to the water-bath which had established equilibrium of temperature. At the end, the cap and stopper were removed from the working tube, and the corresponding tare from the right pan, and the balance made to vibrate two or three times to obtain the exact value of the weight to be determined. A similar method was used for the water receptacle and the U-tubes, which were tared next. During one of the periods of rest involved in the tarings, the gas lamp under the copper wire gauze tube was lighted, and the hydrogen allowed to stream through the hot tube till all the oxygen and moisture of the gauze could be assumed to be removed. Only then the vitriol tube H was attached to the end of the copper gauze tube, and the apparatus thus made ready for the joining on of the reduction-tube and the water receptacle. The outlet of the last U-tube S had a long india-rubber tube attached to it, so that any gas that streamed out there could be collected over water in a graduated Pisani bottle (Fig. 1) provided for the purpose. The joints between P and R, and between R and S, were made with best india-rubber tubing in such a way that the two glass tube ends within the india-rubber almost touched each other, and the joint secured on both sides by ligatures of copper wire.

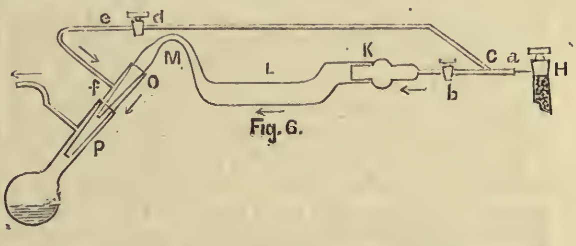

Fig. 6.

(To be continued).

# A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD.*

By F. C. KNIGHT.

A TECHNICAL method for the volumetric determination of lead, requiring but an ordinary amount of manipulation and occupying a short space of time, has long been desired. A number of such methods have been suggested from time to time that promised more or less success. Of these there are but two which give results that are sufficiently accurate even for technical work, a brief outline of which will be given.

The first, which is the more practical, consists of neutralising the nitrate of lead solution with ammonia or carbonate of ammonia, then adding an excess of acetate of sodium, and effecting the titration with a standardised solution of bichromate of potassium, the end reaction being indicated by a red colouration on bringing a drop of the lead solution in contact with a drop of a neutral solution of nitrate of silver. With careful manipulation this process yields good results. The greatest objection to be brought against the method is the uncertainty of the complete precipitation of the lead as the chromate if special precautions are not observed; the length of time involved in the process, and, finally, the ease with which the end-point of the reaction can be overstepped.

The other method consists in precipitating the lead as carbonate from its solution, dissolving the precipitate in a measured quantity of normal nitric acid, to which then a neutral solution of sulphate of sodium is added. The sulphate of lead is precipitated and an equivalent amount of nitrate of sodium formed. The free nitric acid is subsequently determined with a normal alkali solution, the lead percentage being calculated from the observed difference between the original amount of nitric acid used and that found to be still free. This plan requires the lead solution to be quite free from other elements, for which special precautions are necessary, and the length of time involved in the operations quite unfits the process for technical laboratories.

There is another method which has been lately described, which, while not volumetric, appears to offer great advantages over the preceding ones. It consists in dissolving the sulphate of lead in an ammonium chloride solution, and precipitating the lead from the same in the metallic form by means of sheet aluminum, the lead finally being weighed. The results appear to be very accurate. The existing prejudice in technical laboratories against any method which involves a gravimetric determination will, however, operate as a bar against its general introduction if a method equally as accurate, or sufficiently so for all purposes, but volumetric, can be found.

The method about to be described is offered in the hope that it will meet the required conditions. It is based on the formation of oxalate of lead, the decomposition of this salt by sulphuric acid, the determination of the liberated oxalic acid by permanganate of potassium solution, and the calculation of the lead percentage from the amount of oxalic acid with which it was originally combined.

It is not claimed that the idea on which this scheme is founded is new: in fact, a method along similar lines was proposed by Hempel, it being also stated by him that the results obtained were not absolutely accurate owing to the solubility of the oxalate of lead, which error, however, could be reduced to within the limits of 1 per cent by careful manipulation.

Fresenius, in discussing the solubility of oxalate of lead in water, states it to be distinctly greater than that of sulphate of lead, the solubility being still further increased by the presence of ammonia and ammonium salts.

A large number of experiments, instituted for the purpose of determining how the solubility of the oxalate of lead in water could be overcome, showed eventually that while it could not be entirely nullified, it could be reduced to its minimum by effecting the precipitation from an aqueous solution of the lead salt containing about an equal bulk of 95 per cent alcohol, only the slightest traces of lead remaining in solution under such a condition. Further experiments demonstrated that the precipitation was equally complete in the presence of free acetic acid which had been added to the alcoholic solution.

To a neutral solution of nitrate of lead measuring about 20 c.c., an equal volume of 95 per cent alcohol and 5 c.c. strong acetic acid were added, and the lead precipitated by oxalic acid. The precipitate was filtered, well washed with hot water, and the filtrate saturated with hydrogen sulphide gas. A slight brown colouration was noticed in the course of time, but a precipitate of sulphide of lead failed to appear even after the solution had stood for several days.

This experiment was repeated a number of times with the same result, giving thus the assurance that the error due to the excessively slight solubility of the oxalate of lead, under conditions formulated, would not act as a disqualification of a technical method which was based on its use.

The oxalate of lead precipitated from cold alcoholic solutions comes down as a heavy white flocculent precipitate, which settles quickly on agitating the solution either by stirring or shaking, leaving the supernatant liquid perfectly clear. From heated solutions the precipitate falls as a brilliant crystalline powder. The composition of the salt is, however, in both cases the same, its formula being $PbC_2O_4$, containing 70·18 per cent of lead.

The crystalline precipitate filters rapidly and is easily washed; the flocculent variety becomes reduced in bulk and crystalline on being washed with hot water. It is advisable to precipitate the oxalate from the solution which has been heated to 65° C.

Pure lead having been prepared by reduction from C. P. acetate of lead, freeing the regulus from mechanical impurities, and rolling it into thin sheet lead, varying quantities were weighed out to determine the accuracy of the method under consideration.

The standard of the permanganate of potassium solution containing 1·58 grms. of $KMnO_4$ to the litre was established as follows:—3·65 grms. C. P. crystallised oxalic acid were dissolved in 500 c.c. distilled water, from which three separate portions of 25 c.c. each were taken, 5 c.c. concentrated sulphuric acid added, and the titration performed with the previously prepared permanganate solution. There were used in:—

| Experiment. | Oxalic acid. C.c. | Cryst. xalic acid. Grm. | $KMnO_4$. C.c. |
|---|---|---|---|
| 1 .. .. | 25 | 0·1825 | 58·30 |
| 2 .. .. | 25 | 0·1825 | 58·35 |
| 3 .. .. | 25 | 0·1825 | 58·40 |

Making an average of 58·35 c.c. of permanganate solution used, or 1 c.c. $KMnO_4$ solution = 0·003127 grm. $C_2H_2O_4,2H_2O$, from which by the simple stöchiometrical calculation, 1 c.c. $KMnO_4$ solution = 0·00513 grm. lead, in the form of oxalate.

The standard being established, a portion of lead was weighed out and dissolved in 3 c.c. concentrated nitric acid, diluted with 10 c.c. hot water, and carbonate of sodium in slight excess added. The precipitate was dissolved by the addition of 5 c.c. strong acetic acid, 20 c.c. of 95 per cent alcohol being then added to the solution. This was heated to 65° C. and the lead precipitated by adding 10 c.c. of a saturated solution of oxalic acid, the precipitate, after settling, being filtered and thoroughly washed with hot water. The lead oxalate was now rinsed from the filter into a beaker, 50 c.c. hot water and 5 c.c concentrated sulphuric acid added. The solution was warmed to about 65° C., and the titration on the freed

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* A Paper read before the Colorado Scientific Society, Nov. 7, 1892. From the *Journal of Analytical and Applied Chemistry*, vi., No. 11.

oxalic acid effected. Ten determinations were made, the results being :—

| Exp. No. | Weight of lead taken. Grm. | $KMnO_4$ used. C.c. | Weight of lead found. | Per cent obtained. |
|---|---|---|---|---|
| 4.. .. | 0·05392 | 10·4 | 0·05335 | 98·94 |
| 5.. .. | 0·10150 | 19·7 | 0·10106 | 99·56 |
| 6.. .. | 0·15266 | 29·7 | 0·15236 | 99·80 |
| 7.. .. | 0·20878 | 40·6 | 0·20827 | 99·75 |
| 8.. .. | 0·25540 | 49·7 | 0·25496 | 99·82 |
| 9.. .. | 0·30016 | 58·5 | 0·30010 | 99·97 |
| 10.. .. | 0·35204 | 68·6 | 0·35191 | 99·96 |
| 11.. .. | 0·40290 | 78·4 | 0·40219 | 99·82 |
| 12.. .. | 0·45252 | 88·2 | 0·45246 | 99·98 |
| 13.. .. | 0·49876 | 97·1 | 0·49812 | 99·89 |

The average percentage obtained being 99·749.

In order to establish comparisons on a basis which would be of greater value, in that the determinations would be made under conditions necessary in the carrying out of the method on ores and metallurgical products, another series of experiments was instituted, the lead taken for the analysis being brought into the solution, and re-converted into metallic lead, from which point on the process was as above described.

The precipitate of metallic lead from hydrochloric acid solutions was found to be easily, as well as completely, effected by means of pure granulated zinc, the article used having been made by Merk, the granules being of a diameter small enough to allow them to pass through a screen containing 30 meshes to the linear inch. Investigation proved it to be free from lead.

Dilute hydrochloric acid has no action whatever on metallic lead, and even boiling concentrated hydrochloric acid scarcely attacks it. From dilute solutions of pure sulphate of lead in hydrochloric acid granulated zinc precipitates the lead quickly as a sponge, which is easily washed.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, February 16th, 1893.*

Prof. A. CRUM BROWN, F.R.S., in the Chair.

(Concluded from p. 118).

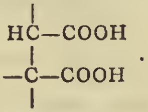
*117. "*Electrolysis of Sodic Ethylic Camphorate.*" By J. WALKER, D.Sc.

By electrolysing sodic ethylic camphorate, prepared by the direct union of camphoric anhydride and sodium ethoxide, the author has obtained the ethylic salts of two new acids, $C_8H_{13}\cdot COOH$ and $C_{16}H_{28}(COOH)_2$, which he proposes to term *campholytic acid* and *camphothetic acid* respectively.

*Camphothetic acid* is a colourless crystalline solid melting at 132°. It behaves as a saturated bibasic acid, forming well-characterised crystalline salts.

*Campholytic acid* is a monobasic unsaturated acid. It boils at 240—242°, and is lævorotatory. Its ethylic salt boils at 212°, and is dextrorotatory. Both readily take up bromine in the cold, forming dibromides. The dibromo-acid, $C_8H_{13}Br_2\cdot COOH$, is a white crystalline solid which melts at 110°. Its alkaline salts at once decompose in aqueous solution according to the equation $C_8H_{13}Br_2\cdot COONa = C_8H_{13}Br + CO_2 + NaBr$, the compound $C_8H_{13}Br$ being unsaturated, readily uniting with bromine in the cold.

It is pointed out that from the nature of the electrolysis and the above-mentioned decomposition of the dibromo-acid, camphoric acid itself must contain the group—



$$\begin{array}{l} \;| \\ HC{-}COOH \\ \;| \\ {-}C{-}COOH \\ \;| \end{array}$$

DISCUSSION.

Dr. COLLIE having pointed out that the method by which Dr. Walker had obtained campholytic acid was such that there was little probability any fundamental change occurred in the camphoric molecule during the process, Dr. ARMSTRONG said that electrolytic oxygen was probably by no means a mild agent, and he thought that in the present instance, as well as in the cases studied by Crum Brown and Walker, it was not improbable that the change was brought about by oxidation: the formation of unsaturated acids especially favoured this view, as these might be regarded as resulting from the displacement of carboxyl by hydroxyl and the subsequent separation of water, or an analogous set of changes. Dr. Walker's ingenious application of Fittig's conclusions was open to question, on the ground that we knew very little at present of the behaviour of closed chain bromo-acids; moreover, the fact that camphoric acid did not yield a fluoresceïn appeared to preclude the idea that camphoric acid was an acid of the succinic type. He was of opinion that, on the whole, the evidence was in favour of the view that camphoric acid was an acid of the glutaric type, and that Dr. Walker's acid was probably a tetrahydrometaxylene derivative containing the carboxyl in one of the methyls.

Dr. WALKER, in reply to Dr. Armstrong, stated that he did not consider it probable that the formation of either the synthetic or unsaturated ethereal salts during the electrolysis was due to oxidation at the anode. Murray had shown in the case of the electrolysis of potassium acetate that there was no sort of proportionality between complete oxidation to carbonic anhydride and "partial oxidation" to ethane, as might be expected if the formation of ethane was due to oxidation. The conditions of the electrolysis found most favourable for the production of synthetic products were such as would almost ensure complete oxidation of the dissolved substance if the primary action was the decomposition of water into oxygen and hydrogen.

*118. "*The Hydrates of Hydrogen Chloride.*" By S. U. PICKERING.

The determinations of the densities of solutions of hydrogen chloride made by Kolb, and also some made by the author, show a strongly marked break indicative of the presence of a trihydrate. They are represented by an appreciably straight line from 0 per cent up to the composition of that hydrate (40 per cent), after which the deviation from straightness is very considerable. On performing a series of freezing point determinations the trihydrate was obtained in large transparent crystals melting at −24·9°; this melting point is lowered by the addition of excess either of water or of acid. This hydrate and the dihydrate, already isolated by Pierre and Puchot, are the only crystalline hydrates which were obtained.

The densities indicate the existence of a change of curvature of a very minor character at a point corresponding to the composition of a hexhydrate, and similar indications are noticeable both in Berthelot's and Thomsen's heat of dissolution determinations. The author's freezing point determinations can afford no evidence for or against such a hydrate, on account of there being a change in the crystallising substance at the point in question, but they indicate the existence of a decahydrate. Roscoe and Dittmar's determinations of the influence of pressure on the composition of the boiling acid suggest the presence of an octohydrate. It seems, therefore, probable that these three hydrates exist in solution, and that they are comparatively stable, as solutions of acid of strengths between the hexhydrate and the decahydrate may be distilled with very little change in spite of great variations in pressure, and are altered in composition to a very small extent by the passage of a current of air through them at temperatures between 0° and 100°.

119. "*A New Base from Corydalis Cava.*" By JAMES A. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

The authors describe under the name of *corytuberine* a new alkaloid which they have obtained by exhausting crude corydaline with hot water; it crystallises from a hot aqueous or alcoholic solution in beautiful silky needles, soluble in cold solutions of sodium hydrate and ammonia, moderately soluble in benzene, and nearly insoluble in ether and chloroform. When heated it begins to blacken about 200°, and then slowly decomposes without melting. Its aqueous and alcoholic solutions are slightly dextrorotatory. Analyses lead to the formula $C_{19}H_{25}NO_4$. The *chlorhydride*, $C_{19}H_{25}NO_4 \cdot HCl$, is obtained in small, well-formed, rhombohedral crystals when a solution of the base in chlorhydric acid is evaporated to dryness. The *sulphate*, $(C_{19}H_{25}NO_4)_2 \cdot H_2SO_4$, is obtained by the interaction of the chlorhydride and the calculated quantity of silver sulphate. The *platinichloride*, $(C_{19}H_{25}NO_4)_2 \cdot H_2PtCl_6$, is precipitated in the form of a pale yellow crystalline powder, slightly soluble in water, on adding hydrogen platinichloride to a solution of the chlorhydride in water. Corytuberine is only soluble to a slight extent in methyl iodide, but the methiodide, $C_{16}H_{25}NO_4 \cdot CH_3I$, can be prepared by digesting an alcoholic solution of the alkaloid with methyl iodide during several hours.

When treated with concentrated solution of hydrogen iodide, one molecular weight of corytuberine gives two molecular proportions of methyl iodide, showing that only two of the oxygen atoms are present as methoxy-groups; corydaline, on the other hand, has all its four oxygen atoms in this form of combination.

The authors also give some notes on yet another alkaloid which they consider to be distinct, not only from corydaline and corytuberine, but from all the bases of *Corydalis cava* hitherto described.

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### *Extra Meeting, February 20th, 1893.*

The Right Hon. Lord PLAYFAIR, K.C.B., LL.D., F.R.S.,
Vice-President, in the Chair.

### *Kopp Memorial Lecture.*

120. "*The Life Work of Hermann Kopp.*" By T. E. THORPE, D.Sc., F.R.S.

Kopp was barely 32 years of age when, so far back as 1849, he was elected a Foreign Member of the Society. Born October 30, 1817, at Hanau, at 18 he proceeded to Heidelberg, where he studied chemistry under Leopold Gmelin. He graduated at Marburg in 1838, the thesis which he presented being on "A Method of Pre-determining the Density of the Oxides," a proof that he had already, when barely 21 years of age, been attracted by the problems which were to constitute the chief experimental labours of his life. From Marburg he went to Giessen, where, at Liebig's instigation, he studied the mode of decomposition of mercaptan by nitric acid, practically the only investigation in pure chemistry that Kopp ever published.

In 1841 he became Privat-Docent at Giessen, and was appointed Extraordinary Professor in 1843. In 1852, on Liebig's removal to Munich, Kopp and Will were together made Ordinary Professors, but after a year he resigned the whole control to his friend and colleague, continuing, however, to work in the laboratory. He remained at Giessen nearly five-and-twenty years, and all his most important experimental work was done there. In 1863 he accepted a call to Heidelberg, and repeated attempts to induce him to accept a position elsewhere were unavailing; "even Bunsen alone," he was wont to say, "keeps me fast in Heidelberg."

Kopp is best known to the literary world by his "History of Chemistry," the first volume of which appeared in 1843, and the fourth and last in 1847. Hofmann, his life-long friend, has told us that by the publication of this classical work, Kopp—then barely 30 years old—suddenly found himself famous. Much of the later historical matter he published grew out of materials collected for the preparation of an enlarged and improved edition of the great work, which Kopp postponed year after year in the hope of being able to make a further study of certain special periods.

On the death of Berzelius, in 1848, the leaders of the Giessen School determined to carry on the work which had mainly occupied the closing years of his life, and established *Liebig and Kopp's Jahresbericht*, which Kopp continned to edit until 1862. In 1851 he joined Liebig and Wöhler in the production of the *Annalen der Chemie und Pharmacie*, and his name appears on the title page of no fewer than 190 volumes of this famous periodical. He also found time to write his "Introduction to Crystallography," the section on Theoretical Chemistry in Graham Otto's *Lehrbuch*, and not a few minor essays.

As an investigator, he occupies an almost unique position, the one consistent purpose of his work having been to establish a connection between the physical and chemical nature of substances—to prove, in fact, that all physical constants are to be regarded as functions of the chemical nature of molecules. When he began his enquiries very few boiling-points were known even approximately; the thermal expansions of barely half-a-dozen liquids had been measured, and the very methods of making such measurements with precision had to be worked out. In fact, at the outset of his investigation, he found the physical constants with which he was more immediately concerned very much as Berzelius found Dalton's values of the relative weights of the atoms.

His more important memoirs naturally fall into comparatively few groups, viz., (1) those concerning the relations between the relative densities of substances and their molecular weights; (2) those treating of the relations between boiling-points and chemical composition; and (3) those relating to the specific heats of solids and liquids.

In nothing was his originality and ingenuity more strikingly manifest than in the construction of his apparatus; to a great extent he was his own instrument maker, and his materials were for the most part glass and cork; but no Japanese worker with his few and primitive tools ever produced results which in point of delicacy, finish, and accuracy surpassed those which Kopp obtained by means of his simple contrivances.

In discussing Kopp's various investigations, Professor Thorpe first considers his work on specific heats and its bearings.

His observations on the relation of boiling-point to composition are next discussed, and the various later observations of other enquirers are taken into account.

Kopp's researches on specific volumes form the last section of the lecture, this subject being dealt with in a very comprehensive manner, not only Kopp's work, but also that of subsequent observers, being fully taken into account, the historical development of the subject being explained and abundantly illustrated.

It is pointed out that by the examination of the very large quantity of experimental material which is now before us, we are driven to the conclusion that molecular volume is not a purely additive property. There is no longer room for doubt that the molecular volumes of substances are affected by far more conditions than we have hitherto taken cognizance of. The value $CH_2=22$ has no other significance than as expressing the average increment in volume in successive members of an homologous series: it is doubtful whether even this mean value is correct; later observations appear to show that the value augments as the series is ascended. The relation $C = 2H$ no longer applies to carbon compounds in general. What is true of carbon and hydrogen is equally true of oxygen, whether as carbonyl or as hydroxyl oxygen: no definite or uniform values can be assigned to oxygen such that the molecular volume of a liquid can be *a priori* determined. The values given by Kopp are simply mean values, but the actual volumes are affected by conditions of which as yet we have no very precise knowledge or any certain means of measuring. The values for other elements are affected by the same considerations: that of chlorine, for example, as it is obtained on the assumption that the values for carbon and hydrogen are constant.

At the conclusion of this section reference is made to Kopp's critical memoir on the subject, published in *Liebig's Annalen* shortly before his death, discussing the outcome of the various researches which followed his own: we rise from its perusal, says the lecturer, with the conviction that after all the work summarised takes us but little beyond the threshold of the fundamental truth of which Kopp was the first to perceive the indication.

Lord **Playfair**, in the course of his remarks at the conclusion of the lecture, mentioned the fact that he had known Kopp fifty-two years ago—they were pupils together under Liebig. He was with him when he was making his first specific volume determinations, and Kopp daily came to him to discuss the results. In the historical survey given by the lecturer there seemed to be one name missing, that of Dalton; it was by reading a memoir by Dalton on specific volumes of solutions—a memoir which was rejected by the Royal Society and published privately—that he had been led to pay attention to the subject: this memoir was full of suggestion.

Dr. **Gladstone** had known Kopp as far back as 1847 to 1848, when he worked in Liebig's laboratory. Kopp's individuality undoubtedly in those days exercised a strong influence over the students.

Professor **Rücker** spoke of the publication of memoirs describing the life work of men like Kopp and discussing its bearings and development as a very happy idea on the part of the Society and as likely to be of great value to scientific workers.

### *Hofmann Memorial Lecture.*

An extra meeting of the Society will be held on Friday, May 5th, 1893, the anniversary of the death of A. W. von Hofmann, when addresses will be delivered by the Right Hon. Lord Playfair, K.C.B., F.R.S., V.P.C.S.; Sir F. A. Abel, C.B., F.R.S., V.P.C.S.; Dr. W. H. Perkin, F.R.S., V.P.C.S.

## PHYSICAL SOCIETY.

### *Ordinary Meeting, March 10th, 1893.*

Prof. A. W. Rücker, F.R.S., President, in the Chair.

**Mr. W. Williams** was elected a member of the Society.

Dr. C. V. **Burton** read a paper "*On the Applicability of Lagrange's Equations of Motion to a General Class of Problems, with special reference to the Motion of a Perforated Solid in a Liquid.*"

The paper shows that to apply Lagrange's equations it is not always necessary that the configuration of the system should be completely determined by the coordinates, but that under certain conditions one need not consider whether the whole configuration is determined by the nature of the known co-ordinates, nor enquire what is the nature of the ignored co-ordinates. The result, which is arrived at by the aid of the "principle of least action" and the investigation given in Thomson and Tait's "Natural Philosophy" (2nd Ed., Part I., Sec. 327), is expressed by the following proportion. If the kinetic energy of a material system can be expressed as a homogeneous quadratic function of certain generalised velocities, $\dot{\psi}$, $\dot{\phi}$, . . . only, the coefficients being functions of $\psi$, $\phi$, . . . only, and if this remains always true so long as the only forces and impulses acting are of types corresponding to $\psi$, $\phi$, . . . , the equations of motion for the co-ordinates $\psi$, $\phi$, . . . may be written down from this expression for the energy in accordance with the Lagrangian rule.

The author then applies the proposition to the case of a perforated solid with liquid irrotationally circulating through the apertures, and shows how it may be extended to any number of perforated solids. The results are not put forward as new, but the method of proof is believed to be different from anything given before. Mr. Bryan had recently given a direct hydrodynamical proof, but the author thought it desirable that the problem should be rigorously treated by the method of generalised coordinates, avoiding any assumptions as to the impulse of the cyclic motion, and proceeding entirely from the principles established by Lagrange and extended by Hamilton, Routh, and Hayward. Incidentally it is mentioned that in equations $(10)^{\text{v.}}$ and $(10)^{\text{vi.}}$ (Thomson and Tait, Part I., Section 327), the sign $\delta v/\delta\psi$ should be reserved. A difficulty which arises in applying the result of Section 319, Example G, in the same work to the motion of solids through liquids is also referred to.

A Criticism by Mr. A. B. **Basset** on Mr. Bryan's recent paper, and also on Dr. Burton's paper, was read by Mr. **Elder**.

Mr. Bassett regards the process employed by Mr. Bryan in obtaining the equations of motion as a distinctly retrograde step, and thinks the most scientific way of dealing with dynamical problems is to avoid the unnecessary introduction of any unknown reactions. The advantages of the theory of the impulse are described by Mr. Basset, and the parts which require care when applying the theory to cyclic irrotational motion pointed out. Comparisons are then made as regards simplicity, between the different methods of treating the subject which have been used by Mr. Bryan, Prof. Lamb, and himself.

With reference to Dr. Burton's paper, he thinks it will tend to complicate rather than elucidate the subject.

An account of how Lagrange's original equations had been modified by Hamilton, Routh, and himself is given at some length, and the advantages and power of the mixed transformation which he had developed are pointed out.

Prof. **Henrici** said he agreed with Mr. Basset in preferring the more general method, but thought the independent treatment of optical problems, as given by Mr. Bryan and Dr. Burton, very desirable.

Dr. **Burton**, in reply, said he concurred with Mr. Basset on some points, but thought it decidedly advantageous to look at problems from different points of view. The investigation he (Dr. Burton) had given was applicable to any number of solids, and, on the whole, simpler than Mr. Basset's.

The **President** pointed out that no attack had been made on the validity or accuracy of Mr. Bryant's or Dr. Burton's work. As to simplicity of the various methods, different opinions might be expected to exist. He himself thought it very desirable that such problems should be approached from different sides.

Prof. G. M. **Minchin** read a paper on "*The Magnetic Field of a Circular Current.*"

Since the magnetic force at any point is the curl of the vector potential at that point, the latter quantity had been calculated for any point P in space. Taking the axis of the circle as the axis of $z$, the line through the centre of the circle and the foot of the perpendicular from P on the plane of the circle as the axis of $x$, and the line perpendicular to $x$ and $z$ as that of $y$, it was shown that the only component of the vector potential is G, parallel to $y$, and that $G\alpha$ is constant along a line of force, $\alpha$ being the $x$ co-ordinate of P. The expression for $G\alpha$ is—

$$G\alpha = i\rho\left\{2(K-E)-k^2k\right\},$$

where $i$=strength of current, $\rho$ and $\rho'$ the distances of P from the furthest and nearest points of the circle, $k^2 = 1 - \frac{\rho'^2}{\rho^2}$, and K and E complete elliptic integrals of the first and second kinds with modulus $k$. The quantity in brackets being a function of $\frac{\rho'}{\rho}$ only, $G\alpha$ may be written in the form $i\rho f\left(\frac{\rho'}{\rho}\right)$, which shows that at all points for which $\rho'/\rho$ is constant, $G\alpha$ varies directly as $\rho$. Since the lines of force in all planes passing through the axis of the circle are the same, attention need only be paid to that containing the point P. The locus of points for which $\rho'/\rho$ is constant is then a circle, whose diameter is the line joining the points which divide the diameter of the circle in which the current flows, internally and externally in the given ratio, and this circle cuts the one described on the diameter of the current circle, orthogonally. A series of such circles corresponding to different values of $\rho'/\rho$ are then drawn, and the values of $2(K-E)-k^2K$ calculated for each by aid of a table of Elliptic Integrals. Denoting these quantities by Q′ then $G\alpha = i\rho Q'$; hence $i\rho Q'$ is constant along a line of force. If P be taken on one of the circles for which the value $Q'$ is $Q'_0$, then the point $P_1$ at which the line of force through P cuts the circle whose constant is $Q'_1$, can be found from the equation $\rho_1 Q'_1 = \rho_0 Q'_0$, for since $\rho_0$, $Q'_0$, and $Q'_1$ are known, $\rho_1$ is easily determined, and the position of $P_1$ plotted. The circles above described also serve for drawing the lines of equal vector potential, and through a mistake in calculation the method of drawing the lines explained in the printed proof of the paper is one which gives the vector potential lines instead of the lines of force.

The author points out that the fundamental definition of vector potential is unsatisfactory, for it leads to the result that the vector potential is infinite at every point in the field of a long straight current. A way of avoiding the difficulty by only considering *differences* of vector potential is described. In the latter part of the paper a complete expression for the conical angle subtended by a given circle at any point in space is worked out, and the result given in terms of two complete elliptic integrals of the third kind, the parameter and modulus of one being $\frac{2\nu}{2-\nu}$, and $k$, respective, and those of the other $\frac{-2\nu}{1+\nu}$, and $k$. The value is—

$$2\pi - \frac{z}{\rho r}\left\{\frac{r+a}{1-\nu}\Pi\left(\frac{2\nu}{1-\nu},k\right)+\frac{r-a}{1+\nu}\Pi\left(\frac{2-\nu}{1+\nu},k\right)\right\}$$

where $\rho$ and $k$ have the same meanings as before, $z$ is the $z$ co-ordinate of P, $a$ the radius of the circle, $r$ the distance from P to the centre of the circle, $\nu$ the size of the angle between the radius vector $r$ and the axis of the circle, and $\Pi(\ )$ elliptic integrals of the third kind.

Prof. Perry thought the problem had been very prettily worked out, and hoped Prof. Minchin would be able to extend the solution to cylindrical coils,—a subject in which he (Prof. Perry) had long been interested.

Mr. Blakesley read a note by Mr. Niven pointing out that the locus of points for which the ratio $\rho'/\rho$ is constant was an anchor ring.

Prof. Minchin maintained that the locus was a sphere, and on this subject a short discussion arose, in which the President, Prof. Perry, Prof. Minchin, Dr. Burton, and Prof. S. P. Thompson took part.

Dr. Sumpner described a method of drawing the lines of force of a circular current, or of any circuit, symmetrical about an axis, by a purely experimental and graphical process. The strengths of field were first determined at several points in the plane of the current, and from these results the points through which lines of force were to pass in order that their distribution might indicate the strength of the field at all points were graphically deduced.

A paper on "*The Differential Equation of Electric Flow*," by Mr. T. H. Blakesley, was postponed.

## CORRESPONDENCE.

### SEPARATION OF WOOL AND COTTON.

*To the Editor of the Chemical News.*

Sir,—Cotton and wool may be separated from each other by operating on two samples of the textile material, using a solution of caustic soda in one case and dilute sulphuric acid in the other case. On boiling, the wool will be removed in the first case, whilst the cotton will be left; in the second case, the cotton will be removed, whilst the wool will be left. The fibres are then in a condition fit for further examination if required.

If a sample be heated for some time to 280° F., the wool can be rubbed out as dust, whilst the cotton will only be rendered slightly tender. Of course, in this case the character of the wool as regards staple, &c., will be lost.

If a sample be dipped into dilute sulphuric acid and hung up for some time in a warm place, the cotton will be destroyed; on washing and drying, the weight of wool is obtained. The loss is due to cotton, size, starch, mineral matter, &c.

Undyed mixtures may be boiled in a weak solution, say, of eosine; wool takes a faint pink colour, the cotton is unaltered. Dyed mixtures may in most cases be recognised by the action of dilute acids; especially if dyed in the piece, and in many cases if dyed in the hand.—I am, &c.,

Thos. T. P. Bruce Warren.

### NOMENCLATURE OF MILK ALBUMENOIDS.

*To the Editor of the Chemical News.*

Sir,—Dr. Halliburton has proposed to give the name "caseinogen" to that albumenoid of milk hitherto known as casein, and to reserve the name casein for the curd produced by the action of rennet on "caseinogen." There are very serious objections to this nomenclature; it is inadmissible, etymologically, to combine the Latin word casein with the Greek root gen. Moreover, the termination gen is not here used in its proper pristine sense. In the words hydrogen and chromogen, for instance, it signifies that these compounds form integral parts of water and colour respectively, and not that a certain decomposition product can be obtained from them. In the word "caseinogen," and its kinsman "fibrinogen," a totally different meaning is given to the termination. Nowadays, it is true, that the etymology of a word matters little, and were there not other objections to the use of the word, it might pass. The name "casein" for the parent compound has the claim of priority, one might almost say of antiquity, while the reservation of the name for a secondary product, which has small chemical claims to be placed in the class of albumenoids to which the termination "in" belongs, is unjustifiable.

As the name "caseinogen" has not been adopted, except by the school of which Dr. Halliburton is the worthy head, may I appeal through your columns to him and his associates to re-consider the question of nomenclature? If I may be permitted, I would suggest the name "chymo-dys-caseose" for the curd produced by rennet; "chymo" expresses that it is produced by rennet, and "dys" shows its analogy to the so-called casein-dyspeptone.

I would further suggest the following system of naming the derivatives of casein:—Those produced by rennet, chymo-dys-caseose and chymo-proto-caseose; those produced by pepsin, pepto-proto-caseose, &c., and pepto-caseone; and those produced by the pancreatic ferment, trypto-proto-caseose, &c.; for the caseose produced by the action of acids, hydrolo-caseose might be adopted. I put forward these suggestions for consideration; the system, which is expressed in the words themselves, might be extended to other albumenoids.—I am, &c.,

H. Droop Richmond.

50, Clanricarde Gardens, Bayswater,
March 13, 1893.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 9, February 27, 1893.

**Physical Properties of Melted Ruthenium.**—A. Joly.—This memoir will be inserted in full.

**Determinations of the Atomic Weight of Lead by Stas.**—G. Hinrichs.—The author asserts that Stas has not succeeded in determining the atomic weight of lead, and considers that if he had operated upon 15—25 grms. of lead he would have obtained higher results.

**Aldehyds of the Terpenes.**—A. Etard.—The author describes camphenic aldehyd, $C_{10}H_{14}O$, and camphenic acid, $C_{10}H_{14}O_2$.

**Constitution of the Hydrated Alkaline Phenates.**—M. de Forcrand.—A thermo-chemical paper not susceptible of useful abstraction.

**Alkaloids of Cod-Liver Oil, their Origin, and their Therapeutic Action.**—J. Bouillot.—The author includes all the alkaloids of cod-liver oil under the joint name pangaduine. He concludes that they are not the result of any fermentation, but exist in the normal hepatic tissue.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 1, January 5, 1893.

**Trials of Different Methods of Preparing White Wines, and on the Composition of a Red Wine.**—J. A. Müller.—The author concludes that if the wine obtained, by fermenting the mixture obtained on treading entire clusters under foot, is inferior to that from the fermentation of the juice, obtained by expressing the grapes, it is that the latter contains a smaller quantity of acids, of tannin, and of mineral salts than the former.

**New Process for Detecting Foreign Substances and especially Colouring-Matters in Wines.**—M. Marouby.—The author proposes a series of test papers cut into circular discs. On placing on one of the discs a drop of the suspected wine, the spot appears surrounded by a halo of different colours.

*Journal fur Praktische Chemie.*
New Series, Vol. xlvi., Part 4.

**Researches on Substitution in the Aliphatic Series.**—Victor Meyer and Fr. Müller.—This lengthy memoir does not admit of useful abstraction.

**Constitution of Sodium Acetacetic Ether.**—Arthur Michael.—It has been already shown that the change of structure which occurs in acetacetic ether is by no means isolated among organic reactions, but that in such transpositions the true explanation of the phenomenon is to be sought, which has been called tautomerism, desmotropy, or pseudo-form, and also that reactions are often viewed as results of substitutions, whilst they are truly processes of addition. The explanation given by Laar contains a germ of truth, as it connects the phenomenon with a "motile," or, more accurately, with a reactive hydrogen. But by assuming the continuous movement of this hydrogen, Laar has drawn away attention from the true cause. On surveying the known cases of desmotropy it will be found that the question is not concerning a motile hydrogen, but that in the supply of such a hydrogen the equilibrium of the atoms may be disturbed, and a more stable arrangement may be effected. There are also cases where such a transposition of atoms may be effected by the combination of an acid with a basic substance. In this sense there exist altogether under the same conditions no desmotropic or tautomeric substances, but merely desmotropic or tautomeric derivatives of substances which, as soon as they obtain their former conditions by substitution or by removal of the basic or acid constituents, return to their old constitutions by atomic transposition. Certain theoretic conceptions have been already connected with tautomerism, desmotropism, and pseudo-form, and I may therefore be permitted to propose for this phenomenon the name merotropism.

# MISCELLANEOUS.

**Correction.**—We find to our regret that the article by Prof. Hampe on "The Simultaneous Precipitation of Copper and Antimony by the Electric Current," which appeared in the Chemical News, vol. lxvii., p. 103, has, by an oversight, not been credited to the *Chemiker Zeitung*, in which it originally appeared. It is of course our duty to acknowledge this error.

**Researches on Alloisomerism.**—Arthur Michael.—These researches consist of memoirs on the addition of bromine to acetylendicarbonic acid and its ethyl ethers, by A. Michael; on the action of sodium ethylate upon dibromsuccinic ether, by A. Michael and C. C. Maisch; on the crotonic acids and their derivatives, by A. Michael and O. Schulthess; on the formation of solid crotonic acid in the reduction of allo-α-brom- and chlorcrotonic acid, by A. Michael; on the addition of bromine and chlorine to solid crotonic acid, by H. Abbott Michael; and contributions to a knowledge of some homologues of malic acid, by A. Michael and G. Tissot.—*Jour. Prakt. Chemie*, New Series, xlvi., Parts 5—7.

**The Chemical Laboratory of Wiesbaden.**—According to the *Chemiker Zeitung* the Chemical Laboratory of Geh. Hofrath Prof. Dr. R. Fresenius has, during the winter term, been attended by sixty-one students. Of these forty-five are from Germany, five from North America, three from Austria, three from Russia, one from England, one from Holland, one from Belgium, one from Spain, and one from Java. There were three assistants in the tuitional laboratory, four in the Versuchsstation, and seventeen in the various departments of the laboratory of research. The staff, including in addition to the Principal, Profs. H. Fresenius and Borgmann, Drs. W. Fresenius, E. Hintz, Frank, and the architect Brahm, will be augmented by Dr. W. Lenz, lecturer for microscopy. The next term begins on April 24. In addition to scientific work (purely) there have been conducted, during the winter, numerous investigations in the interest of commerce, the arts, mining, agriculture, public health, and justice.

**The Permeability of the Skin for Microbia.**—B. Wasmuth.—The researches which the author has conducted upon himself with *Staphylococcus pyogenes albus* and *aureus*, with *Staphylococci*, and the cocci of erysipelas upon rabbits, guinea-pigs, and white mice, and with virulent splenic fever on guinea-pigs, prove that the healthy, uninjured skin of man and other animals is permeable for micro-organisms. They find entrance along the sheath of the hairs, but not by the sudatory pores. Inunction with microbia mixed with lanoline makes no difference in the nature and the speed of the infection.—*Centralblatt fur Bakteriologie* and *Chemiker Zeitung*.

**The Part Played by Flies in the Dissemination of Cholera.**—J. Sawtschenko.—Whilst we already know from the researches of Celli (*Centralblatt f. Bakteriologie*, 1888, iv., 486), that the bacteria of tubercle, splenic fever, abdominal typhus, and European cholera pass unhurt through the digestive organs of flies, and reappear in their excrements without having forfeited their virulence, similar observations had until the present not been made with the bacteria of Asiatic cholera. The author's researches in this direction have supplied the deficiency and led to the following results:—In the intestines of flies which had been fed on cholera cultures, the bacteria of cholera were easily recognised after periods of twenty-four, forty-eight, seventy-two, and in one case ninety-six hours. In the contents of the intestines of flies, which had been fed not with pure cholera cultures but with excrements, or with the contents of the small intestine of patients who had died of cholera, Koch's cholera bacteria were still to be distinguished after twenty-four, forty-eight, and seventy-two hours along with other bacteria to be met with in the materia used for infection. The cholera bacteria obtained from the intestines of flies did not lose their virulence even after forty-eight to seventy-two hours. In view of these results the author takes up the question whether flies merely disseminate by their excreta the cholera bacteria which they have taken up, or whether the bacteria do not at suitable temperatures and under suitable dietetic conditions of nutriment multiply within the digestive system of the flies. He considers the latter case as the more probable. Hence in this case the flies would not be regarded merely as disseminators of infections, but, in part at least, as its foci from which new, fresh generations of cholera bacteria perpetually arrive upon our food.—*Centralblatt fur Bakteriologie* and *Chemiker Zeitung*.

## MEETINGS FOR THE WEEK.

Monday, 20th.—Medical, 8.30.
—— Society of Arts, 5. "Alloys," by Prof. W. Chandler Roberts-Austen, C.B., F.R.S. (Cantor Lectures).
Tuesday, 21st.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Physical and Psychical Neurology," by Prof. Victor Horsley, F.R.S.
—— Society of Arts, 8. "Newfoundland," by Cecil Fane.
—— Pathological, 8.30.
Wednesday, 22nd.—Society of Arts, 8. "The Manufacture of Non-Poisonous White Lead," by Perry F. Nursey, C.E.
—— Geological, 8.
Thursday, 23rd.—Royal, 4.30.
—— Royal Institution, 3. "The Great Revival—A Study in Mediæval History," by the Rev. Augustus Jessopp, D.D.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8. (Anniversary).
Friday, 24th.—Royal Institution, 9. "Interference Bands and their Applications," by Lord Rayleigh, F.R.S.
—— Physical, 5. "On the Differential Equation of Electric Flow," by Thomas H. Blakesley, M.A. "Experiments on the Viscosity of Liquids," by Prof. Perry, J. Graham, and L. W. Heath.
Saturday, 25th.—Royal Institution, 3. "Sound and Vibrations," by Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1739.

# THE CHEMICAL CONSTITUTION OF THE ATMOSPHERE FROM REMOTE GEOLOGICAL PERIODS TO THE PRESENT TIME.

By Dr. T. L. PHIPSON, F.C.S.,
Formerly of the Univeraity of Brussels,
Member of the Chemical Society of Paris, &c.

The chemical constitution of the atmosphere must have varied in successive ages just as the various flora and fauna of the earth have changed. The presence of combustible substances such as pyrites, molybdenite, copper pyrites, and graphite, in the primitive rocks, long ago appeared to me to point clearly to the fact that if these rocks had been formed by fusion and crystallisation by slow cooling, free oxygen must have been absent from the air.* Again, that carbonic acid must have been present in the atmosphere in much larger quantities than at present during the period of the coal-flora has appeared to many to be proved by the enormous residues of carbon, as compared with the more recent deposits of lignite and peat.

Water and air are considered by most modern authors as the *residues* left after the cooling of the earth—residues of stupendous chemical action, the formation of which residues rendered the globe fit for the existence of organised beings. But was the air in these primitive periods such as we now know it?

In a former paper† I promised to examine the doctrine set forth on this interesting subject by the late Prof. C. J. Koene, of the University of Brussels, in a series of popular lectures to which I have already referred. In order to place this theory on as fair a footing as possible, I shall add some considerations on the respiration of the lower forms of animal life, and will quote Ch. Martins's opinion regarding the compensation theory of Dumas; also Hoefer's reason why plants must have appeared before animals, and Reiset's recent analytical results for carbonic acid in the air of the open country, &c.

I do not wish it to be understood that I endorse Koene's theory as a whole, for it appears to me beyond the realms of even the most advanced science to solve questions of this nature, though he did not think so.

Four great names appear in connection with this subject, Jean Baptiste Dumas and Justus Liebig on the one hand, Berzelius and Mulder on the other. The two former appear to have considered the chemical composition of the atmosphere to be permanently fixed for an indefinite period (and perhaps they admitted it always to have been so since the first appearance of life upon the globe), basing their views upon the fact that whilst plants give out oxygen and absorb carbonic acid, animals absorb oxygen and reject carbonic acid. Dumas and Liebig looked upon the animal and vegetable kingdoms as indispensable one to the other, and believed that their mutual action upon the atmosphere would keep its composition constant. Ch. Martins, a celebrated French naturalist and contemporary of Dumas, criticised this compensation theory by pointing out the extremely minute quantity of air affected by the respiration of plants and animals as compared with the vast bulk of oxygen in the atmosphere. Thus he shows that the atmosphere containing 134,000 cubic measures of oxygen, the entire animal world only consumes in a century 15 to 16 of these cubic measures (this is Dumas's own calculation); hence, says Prof. Ch. Martins, "the constant composition of the air, one of the elements of which, oxygen, is constantly transformed into carbonic acid by men and animals, does not depend upon *a pretended equilibrium between the respiration of plants and animals*, but upon the fact that the quantity of oxygen consumed by animals is out of all proportion to that contained in the entire atmosphere" (*Météorologie et Physique du Globe*).

Berzelius felt convinced that oxygen must gradually *diminish* in quantity in the air, for he declared he knew of *no de-oxidising process sufficiently great and general to set at liberty all the oxygen which combined, every instant, with combustible material* (*Traité de Chimie*).

The great Dutch chemist Mulder goes still further; he insists upon the enormous production of carbonic acid by the respiration of animals, fermentation, volcanic action, and human industry, and notes the constantly increasing destruction of forests, those vast manufactories of oxygen gas. He concludes that *carbonic acid must increase, and that oxygen has continued to decrease since the first appearance of life upon the earth.* With regard to volcanic action I myself have calculated roughly, on the spot, the quantity of carbonic acid produced by a small chalybeate spring near Neubau in the principality of Waldeck (Germany) in the year 1865. It was a little over one pound per hour, or *about a quarter of a cwt. per diem*; and this is only one of thousands of similar springs scattered over the surface of the globe.

Koene upholds a contrary theory, according to which the *carbonic acid and nitrogen of the air have never ceased diminishing since the origin of living creatures, whilst the relative proportion of oxygen has gone on increasing.*

In the more remote geological ages there could have been no free oxygen at the high temperatures to which all combustible bodies were exposed, and we can only conceive the atmosphere, when the earth had cooled sufficiently, to have been composed of nitrogen, carbonic acid, and vapour of water. Such is the starting-point of Koene's doctrine. He admits that when circumstances permitted the existence of living beings, plants (or *protoctista*, let us say, which cannot be classed either as plants or animals)* first appeared and prepared, during a vast lapse of time, the surface of the earth for the existence of higher organisms. These first beings, according to Koene, were *anærobic*: that is, they were capable of existing without free oxygen. It is interesting to note that some fifteen years after this theory was first professed, Pasteur actually discovered anærobic microbes.

It would be easy to admit, with the school of Lamarck and Geoffroy St. Hilaire, that, as circumstances changed, these anærobic protoctista gave rise to *aërobic* beings and plants. Anyhow, to return to Koene's theory, *plants were the first producers of oxygen*, and they produced it in constantly increasing quantities as ages rolled by, until it appears to have attained its greatest proportion during the coal-flora period; the enormous leaves of these plants fed luxuriously on the rich carbonic air, and set free immense quantities of oxygen.

Hoefer's opinion that plants first appeared is exposed in the few lines: "Starting from the theoretical view of the gradation of organised beings, and looking upon *vegetable life as a necessary condition of animal life*, the former must, consequently, have appeared before the latter." Alex. von Humboldt made a very weak attempt to disprove this by alluding to the fact that the Eskimo live almost exclusively on fish and cetacea.

It is quite possible that plants of those remote geological periods might have flourished in an atmosphere so rich in carbonic acid that it would kill plants of our modern period. I have only made very few experiments on this subject, but I hope to make more. In those I have made with such plants as the lilac, the willow, &c.,

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* Some modern writers have supposed that granite has never been heated beyond 500° C., but we find a higher temperature than that in a modern lava when it is comparatively cool.

† "Koene and Stas: Chemistry at Brussels, 1840—1860" (Chem. News, vol. lxvii. p. 51).

* Phipson, "Protoctista, &c." (*Jour. de Médecine*, Brussels, 1861).

I have found that an excess of carbonic acid destroys them, and I cannot yet say whether our modern flora possesses any plants which would thrive in an atmosphere overcharged with carbonic acid.

The next point to which the theory refers is that an immense quantity of carbon is fixed in the earth by the remains of plants and animals, and never returns to the air; at the same time nitrogen is also fixed in like manner, and is extracted daily from the air in vast amounts to form ammonia and nitrates. Oxygen alone remains in relatively larger and larger proportions; it has increased since the first living beings appeared, and, curious to relate, *its maximum corresponds with the maximum development of the central nervous and brain tissue.* As for carbonic acid, it has almost entirely gone. For the last half-century it has been noted as only six, five, and four parts on 10,000 parts of air. The latest determinations by Reiset (a most careful chemist, pupil of Boussingault, and one of the editors of Millon's well-known "Annuaire"), made in the open air at a country place many miles from Paris, gave three parts on 10,000 parts in 1889, and he could not get a fraction more.

One of the most expert chemists of modern times, Pelouze, says on this subject: "On comparing the analyses of atmospheric air undertaken some years ago by Gay-Lussac with those made quite recently [Pelouze wrote in 1848], we recognise that the proportion of oxygen and nitrogen have not varied in that interval. However, as the methods of analysis, though greatly improved, are not absolutely exact, it is quite possible that the composition of the atmosphere is undergoing very slight variations which will only become appreciable after a great number of years" (*Abrégé de Chimie*).

Baudrimont about the same time wrote: "The atmosphere is eminently variable, and whatever means of reparation Nature may employ, it is more than probable that it will change to such a degree as no longer to support life" (*Traité de Chimie*, vol. i.).

Anatomists cannot tell us how respiration is effected in the lowest creatures in the scale of life,—those which are supposed to have been the first produced. They simply say all vestiges of respiratory organs are absent, unless it be the cell wall or outer envelope. They do not say whether these beings require free oxygen or not, though this can be proved for the higher organisms, such as fish and tadpoles, which live in water, and I have found that the minute *Protococcus palustris* carries on its respiratory functions much as the higher organised plants do.* In such animals as *Holothuria tubulosa*, the function of respiration is little, if at all, separated from that of the intestine. Water is sucked in three times a minute, and remains about twenty seconds in the animal's body. It is not yet known whether the lower forms of life may be able to derive oxygen from water or carbonic acid, or both; but it appears evident that oxygen is essential for plants and animals however low in the scale; in fact, oxygen and life seem to be synonymous terms in this respect.

To return once more to Koene's doctrine, it is based, as I have shown, upon the *incomplete eremacausis* of organic matter confided to the earth and protected from the action of the air, by which enormous quantities of carbon and nitrogen have always been and are still slowly being subtracted from the atmosphere. He does not believe that either of these elements can be supplied from without—from cosmic space—and they disappear thus for ever from the air.

Against this view it may be asked, Is this eremacausis or slow combustion incomplete? Is not carbonic acid returning in immense quantities to the atmosphere, not only by the respiration of animals and volcanic action, but by the agency of man himself? In time, the whole of those vast deposits of coal and lignite formerly taken from the air will return as carbonic acid; and if forests continue to be constantly annihilated, as Mulder remarked, to make room for clay and stone buildings, will not carbonic acid increase until it predominates, as it is supposed to have done in primitive times?

Koene has alluded to the coincidence of the higher development of the central nervous system and brain power, with the present increased quantity of oxygen in the air. Man, he says, has become more and more excitable; he now lives faster, prefers intellectual to physical activity, desires shorter hours of labour [this was written in 1856], strives actively for recreation or enjoyment, and rarely, if ever, attains to the age of the patriarchs. Vitality, nervous power, and oxygen have increased together upon the earth from the earliest ages, and the history of this increase can be read by the chemist in the records of the earth's strata.

In conclusion I cannot avoid showing the weak points of this ingenious theory when considered from a purely philosophical aspect. Koene admits oxygen to be the product of life, whilst it is the condition of life, and finally, that its predominance will be the cause of universal death. This is certainly paradoxical; but, as I hinted before, the solution of these problems is probably beyond the powers of Science.

Putney, March, 1893.

# A CURIOUS FORMATION OF THE ELEMENT SILICON.

By H. N. WARREN, Research Analyst.

During the preparation of specimens of crystalline and other forms of silicon, I obtained a most curious formation of that substance which would appear, when treated analytically, to be composed of graphitoidal silicon, constituted so as to form most perfect and well developed crystals consisting of oblique octahedrons. This peculiar modification of the element first made its appearance upon subjecting potassium silicofluoride to a most intense heat in contact with impure aluminium. Upon separating the graphitoidal silicon thus formed by the aid of dilute acids, small quantities of the other substance were observed. Direct steps were at once taken to procure it, if possible, in larger quantities, after numerous experiments had failed to reproduce it. The following method was used with success, although still very uncertain.

Graphitoidal silicon was first obtained by introducing pieces of metallic aluminium about the size of a walnut into a clay crucible of convenient dimension, and subjected to a heat sufficient to maintain in a fused state a mixture of four parts potassium silicofluoride, one of potassium chloride, and two of potassium carbonate. After the violent reaction attending the introduction of the aluminium had subsided, the crucible was urged to whiteness for about five minutes; after cooling and breaking the same, a perfect round button consisting of about 80 per cent silicon was obtained. This, after carefully detaching any adhering slag, was placed in a plumbago crucible in contact with about twelve times as much aluminium as the button originally obtained, together with an addition of two parts by weight of metallic tin, and covered with a layer of sodium silicate. The crucible with its contents were then subjected to the most powerful heat that could be obtained for about two hours. After cooling and breaking the piece of aluminium contained therein, the new modification was obtained in large perfect crystals posssessing a full metallic lustre, and true models of oblique octahedrons.

After dissolving the small quantity of aluminium mechanically entangled, the analysis of the crystals denoted the existence of pure silicon only, being insoluble in all acids, except hydrofluoric acid, and infusible.

In appearance the crystals resemble crystals of cast iron, which are sometimes met with upon breaking a pig

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* Phipson, "Production of Oxygen by *Protococcus Pluvialis*" Chemical News, 1883).

of that substance, the largest assuming a size of over half an inch across the faces, and as perfect as a crystal of alum; in fact, it would be difficult to say as to what dimension these crystals could be obtained, as the author has on more than one occasion obtained perfect models over an inch and a half in length and thickness.

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## RAPID PREPARATION OF CHROME AND MANGANESE AT A HIGH TEMPERATURE.

By HENRI MOISSAN.

Chrome and manganese, for which we indicate in this paper a rapid method of preparation, are most commonly obtained in laboratories by reducing the oxide by means of carbon. Industry has utilised this reaction for producing in blast furnaces larger quantities of ferro-manganese and of ferro-chrome.

The use of the electric furnace enables us to convert these long and difficult reductions into ordinary lecture experiments.

The oxides of nickel and cobalt are also rapidly reduced by means of carbon in the electric furnace. Under these conditions we have obtained cast metals containing:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Ni .. .. | 85·00 | 85·82 | 90·60 | 94·06 |
| C .. .. | 14·59 | 13·98 | 10·20 | 6·35 |

A specimen of cobalt prepared with an excess of oxide gave us in three successive analyses:—

C per cent .. .. .. 0·726 0·732 0·741

*Manganese.*—Pure manganese oxide is mixed with coke and ignited in the arc. On operating with 300 ampères and 60 volts the reduction is complete in five or six minutes. There remains at the bottom of the crucible a regulus of manganese carbide of from 100 to 120 grms.

The reduction is made rather more slowly, requiring from ten to fifteen minutes with a voltaic arc measuring 100 ampères and 50 volts.

On operating in presence of an excess of coke the manganese is saturated with carbon and we obtain cast metals yielding on analysis the following figures:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Mn .. .. | 85·00 | 85·82 | 90·60 | 94·06 |
| C .. .. | 14·59 | 13·98 | 10·20 | 6·35 |

But if the reduction is produced in presence of an excess of oxide, the quantity of carbon decreases much, and in certain ingots we do not find more than from 4 to 5 per cent of carbon. When the cast manganese thus prepared contains only little carbon, the metal may easily be preserved in open vessels; but as soon as the quantity of carbon increases, the moisture of the air quickly decomposes the carbide. Small fragments laid in water are transformed in twenty-four hours, yielding a gaseous mixture of hydrogen and hydrogen carbides.

*Chrome.*—We know that the reduction of chromium sesquioxide by carbon is much more difficult than that of manganese oxide. This operation in the electric furnace requires only from eight to ten minutes if we have at our disposal a current of 350 ampères and 50 volts.

The mixture of ignited chromium sesquioxide and of carbon is easily reduced and leaves a brilliant regulus, perfectly melted, of from 100 to about 110 grms. With a current of 50 volts and 100 ampères the experiment is made on a smaller quantity of substance in fifteen minutes as a maximum.

A current of 30 ampères and 50 volts suffices to yield a regulus of 10 grms. in thirty or forty minutes.

The melted metal adheres to the crucible. According as the quantity of oxide or of carbon predominates, we obtain a metal richer or poorer in carbon. The different specimens obtained under these conditions gave the following figures as their percentage of carbon:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Cr .. .. | 87·37 | 86·25 | 90·30 | 91·70 |
| C .. .. | 11·92 | 12·85 | 9·47 | 8·60 |

If we obtain this cast chrome it may be refined by a second operation. The metallic carbide obtained as above, broken into coarse fragments, is placed in a coke crucible, carefully lined with chromium oxide, and covered with the same oxide. This mixture is submitted anew to the temperature of the electric arc; superficial oxide melts, then the metal enters into fusion and loses by degrees all the carbon which it contains. The chrome thus prepared being heated in a current of chlorine is converted into a volatile chloride without leaving a trace of carbon.

This process renders it possible to obtain metallic chrome rapidly and in a rather large quantity. It does not require a very important outlay if we have at disposal motor power produced by a fall of water, since the dynamo used in these experiments cost only 1200 francs.

This reduction is not effected only with chromium oxide produced in the laboratory; it may also be produced from chrome iron as met with in nature. We then obtained a melted and perfectly homogeneous alloy of iron and chrome. It is easy to convert the chrome of this alloy into a chromate. The alloy, coarsely powdered, is thrown into a melted bath of an alkaline nitrate; there are produced insoluble ferric oxide and alkaline chromate soluble in water and capable of being purified by re-crystallisation.

These experiments have been made at the Conservatoire des Arts et Métiers by the kind permission of Colonel Laussedat.—*Comptes Rendus*, cxvi., No. 8.

## A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD.*

By F. C. KNIGHT.

(Concluded from p. 129).

The lead taken for the following experiments was dissolved in 5 c.c. concentrated nitric acid, 10 c.c. concentrated sulphuric acid added, and evaporated until the sulphuric acid fumes appeared. To the mass, when cool, water was aeded, and the sulphate of lead filtered off, washed first with hot water acidified with sulphuric acid, and finally with hot water alone. The sulphate of lead was then rinsed off the filter into a beaker, 3 c.c. concentrated hydrochloric acid added, and enough water to bring the bulk to about 100. The solution was boiled until the whole of the sulphate of lead was dissolved and 2 grms. of pure granulated zinc added. After an action of five minutes, an additional 0·50 grm. of zinc was introduced, and the solution again brought to the boiling point, when 10 c.c. more of concentrated hydrochloric acid were added. In a few minutes all of the zinc had dissolved. The solution was decanted from the lead sponge, the latter washed, re-dissolved in nitric acid, and the precipitation as oxalate made as before described. The results were:—

| Exp. No. | Weight of lead taken. Grm. | $KMnO_4$ used. C.c. | Weight of lead found. | Per cent obtained. |
|---|---|---|---|---|
| 14.. .. | 0·22150 | 42·9 | 0·22007 | 99·76 |
| 15.. .. | 0·21134 | 40·9 | 0·20981 | 99·32 |
| 16.. .. | 0·20756 | 40·2 | 0·20632 | 99·39 |
| 17.. .. | 0·16683 | 32·5 | 0·16672 | 99·94 |

The average percentage obtained being 99·60.

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* A Paper read before the Colorado Scientific Society, Nov. 7, 1892. From the *Journal of Analytical and Applied Chemistry*, vi., No. 11.

It has been mentioned that when pure sulphate of lead in hydrochloric acid solutions is precipitated with granulated zinc it comes down in a coherent spongy mass. This is, however, not the case when certain impurities are associated with the precipitate, notably bismuth, a not uncommon constituent of our Western ores.

When the sulphate of lead is impure, the precipitated lead comes down in separate pieces which are with difficulty made to cohere, or the complete precipitation may even be prevented. The presence of bismuth especially is likely to prove vexatious and vitiate correct results if proper precautions for its total elimination from the sulphate of lead are not taken. The deportment of bismuth in solutions is so interesting that a mention of its behaviour, where it exists as sulphate, may be of interest.

L. Laurent observes that there exist two sulphates of bismuth, the one soluble and the other insoluble in water. If bismuth be dissolved in boiling nitric acid and sulphuric acid added to the solution, there is at times an abundant precipitate produced, and at others none whatever. The precipitate may be easily soluble in small quantities of water, and again remain entirely insoluble, no matter how much water be used. These phenomena are dependent upon the relative amounts of free sulphuric acid present when the sulphate of bismuth is formed, and the temperature of the solution. If sulphuric acid be added to a cold solution of nitrate of bismuth, care being taken to prevent the mixture from becoming heated, no precipitate will be produced. If an excess of sulphuric acid should have been added, a sulphate of bismuth will be deposited in crystalline needles, which is scarcely soluble in sulphuric acid, but extremely so in water. If, however, a solution of this salt be heated, whether the quantity of water be large or small, a sulphate of bismuth will again be gradually precipitated which is insoluble in either hot or cold water, even if a considerable quantity of sulphuric acid should have been added.

I have found that the difficulty in regard to effecting a complete solution of bismuth may be obviated if, in the treatment of ores and metallurgical products, a large excess of sulphuric acid is added to the nitric acid solution, so that, when the evaporation takes place and the sulphuric acid fumes appear, the mass will still be in a fluid and not in a pasty condition. If the mixture is then allowed to cool, and cold water added gradually to prevent heating, all of the bismuth goes into solution and remains so for a sufficient length of time to allow a filtration and separation from the sulphate of lead to be effected.

Another impurity not unlikely to contaminate the sulphate of lead, if sufficient excess of sulphuric acid is not added, is antimony. Such antimony would also be reduced to the metallic state in conjunction with the lead by the zinc. However, in re-effecting the solution of the lead by nitric acid, the antimony would remain as the insoluble oxide and thus be eliminated.

The following experiments demonstrate that even considerable quantities of bismuth and antimony, when originally present, do not essentially affect the accuracy of the process. Five portions of lead were weighed out, and to these, severally, 100 m.grms. each of metallic antimony and bismuth were added:—

| Exp. No. | Weight of lead taken. M.grms. | KMnO used. C.c. | Weight of lead found. | Percentage obtained. |
|---|---|---|---|---|
| 18 | 215·44 | 41·9 | 214·94 | 99·76 |
| 19 | 232·21 | 45·1 | 231·36 | 99·63 |
| 20 | 258·58 | 50·1 | 257·01 | 99·38 |
| 21 | 244·50 | 47·6 | 244·18 | 99·86 |
| 22 | 250·74 | 48·5 | 248·80 | 99·22 |

The average percentage obtained being 99·57.

In ordinary practice such combinations as given in the experiments just noted are hardly likely to be met with, and the results obtained are an ample demonstration of the sufficient accuracy of the method for all technical purposes.

In the analysis of ores and furnace products the following plan of operation has been found most suitable:—

Place 1 grm. or 0·50 grm., according to richness of the material, in a four-inch casserole; add 15 c.c. concentrated nitric acid and 15 c.c. concentrated sulphuric acid; cover with watch-glass and heat on a hot plate until the decomposition is effected, and the fumes of sulphuric acid appear. Remove and cool; when cool, gradually add about 50 c.c. of cold water, heat to boiling, and immediately filter. Wash well with boiling water slightly acidified with sulphuric acid, and finally with plain hot water. Now rinse the insoluble residue into a beaker of about 200 c.c. capacity, using not more than 50 c.c. water; add 5 c.c. concentrated hydrochloric acid, cover with watch-glass, and boil briskly for five minutes. The sulphates of lead and lime pass into solution.

If much silica and sulphate of barium be present, it is well to filter and wash well with boiling water. If such filtration is undertaken, it must be done rapidly. Small amounts of silica do not interfere, but larger quantities prevent the subsequent precipitation of the lead in one spongy mass.

Dilute the solution with water to about 100 c.c., keeping it hot, but not boiling. Now add 2 grms. of granulated zinc. The lead begins immediately to be deposited as a metallic sponge. When the action of the acid on the zinc has apparently ceased, add an additional 0·50 grm. After five minutes the solution is again boiled for a few minutes, and then 10 c.c. concentrated hydrochloric acid added. This dissolves the remainder of the zinc very quickly, and when the reaction is completed the lead sponge will be found floating on the surface of the liquid. Decant solution, wash the lead sponge with cold water, and press it out flat with the finger. Dissolve it in 1 c.c. concentrated nitric acid and 20 c.c. hot water. Add now a slight excess of carbonate of sodium (the salt is preferable to the solution), and re-dissolve the precipitated carbonate of lead by adding 5 c.c. strong acetic acid; add 20 c.c. of 95 per cent alcohol, heat the solution to 65° C., and precipitate the lead with a saturated solution of pure crystallised oxalic acid. The lead comes down at once as a dense white crystalline precipitate. Stir briskly until the precipitate settles rapidly, leaving a perfectly clear supernatant liquid. Filter and wash precipitate three times with a hot mixture of alcohol and water (1 : 1), and then four times with hot water alone. (In washing the precipitate it is well to use a fine jet, keeping the stream on the filter and not allowing it to flow on the glass, as otherwise the precipitate is apt to creep upon the funnel, and thus occasion loss). When thoroughly washed, the precipitate is rinsed into a flask or beaker with about 50 c.c. hot water, 5 c.c. concentrated sulphuric acid added, and the oxalic acid determined by permanganate of potassium solution in the usual way.

The only precautions to be observed are those which have already been mentioned with reference to bismuth, and when large amounts of silica or sulphate of barium are present.

As the ratio of the atomic weight of lead to that of the combined oxalic acid is very high, any error occurring in the titration will be magnified. It is advisable, therefore, to use quite dilute solutions of permanganate of potassium, the strength of this being not greater than 1·58 grms. $KMnO_4$ to one litre, which will give a strength of solution, 1 c.c. equals about 50 m.grms. of lead.

The standard of the solution in terms of lead is obtained by multiplying the standard in terms of crystallised oxalic acid by 1·6428.

The time involved in the execution of the method on a single assay occupies from thirty-five to forty minutes, and the carrying out of a number of assays simultaneously is easily feasible.

The following results indicate what concordance can be obtained by the method:—

| Exp. No. | | Per cent. |
|---|---|---|
| 23. | Broken Hill ore .. .. .. .. | 27·61—27·50 |
| 24. | Silver precipitate of leaching process .. .. .. .. .. | 28·86—28·75 |
| 25. | Oxidised ore .. .. .. .. .. | 2·56— 2·66 |
| 26. | Galena associated with pyrite and chalcopyrite .. .. .. .. | 22·25—21·95 |
| 27. | Galena ore (gravimetric, 66·75 per cent of lead) .. .. .. .. | 66·58—66·66 |
| 28. | Oxidised ore .. .. .. .. .. | 41·04—41·29 |

## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E.,
and J. B. HENDERSON.

(Continued from p. 127).

After attaching the oxide of copper and the water-receptacles, several litres of hydrogen were allowed to pass through the cold apparatus to make sure of every trace of enclosed air being eliminated, and only then the gas under the reduction-tube was lighted. As soon as the oxide of copper comes up to a certain temperature, which lies below redness, the hydrogen current collapses—the gas being converted completely into water by the first short layer of oxide which it strikes against. While the formation of liquid water progresses, the water-receptacle lies in an ice-bath to minimise the weight of water which passes into the U-tube; but as soon as the oxide appears to be completely reduced, a water-bath of the temperature of the laboratory is substituted, so that as little as possible of the vapour of water in the apparatus is driven out into the air, while the water expands in rising up to the temperature of the balance.

The experiment requires constant attention, but could not be said to be difficult of execution. When all the oxide of copper has apparently suffered reduction to metal, the process is continued for a while to make sure that the reduction really is complete; the lamps under the magnesia bath are then turned off, and hydrogen is allowed to pass through the apparatus until the copper is quite cold. The reduction-tube and the water apparatus are then detached from the rest of the apparatus and prepared for the balance by passing a current of vitriol-dried air through them to expel the hydrogen. The water receptacle is then closed by an indiarubber cap at the outlet end, and by means of a closely fitting though not ground in stopper, as shown by Fig. 4, the reduction-tube by its stopper and cap as explained before, the U-tubes by turning their stoppers. The weighings are effected in the way already explained.

Before attempting a real synthesis we carried out those "blanks" and *quasi*-"blanks" which were detailed in the section on Dumas's work, and, to us, served as useful rehearsals.

The results of our syntheses proper are given in the following table, which includes all the experiments which we made, except one or two which had to be stopped in their middle on account of breakdowns; the table, in other words, includes all those of our experiments which were really completed. In a publication like the present, it is not right to exclude any experiment or experiments, because the result is not to the taste of the experimenter; but, on the other hand, *he* is the only person competent to say which of the results should be "blackened."

As our table gives only the net weights, we will give all the details of one of the experiments:—

*Experiment VIII.*

| | |
|---|---|
| Weight of reduction-tube + oxide of copper.. .. .. .. .. .. | tare + 36·3740 grm. |
| Weight of reduction-tube + metallic copper .. .. .. .. .. .. | tare + 19·2814 |
| Hence, oxygen S, uncorrected | 17·0926 |
| Water-flask after the experiment.. | tare + 25·3239 |
| Water-flask before the experiment | tare + 6·1363 |
| Hence, liquid water.. .. .. | 19·1876 = $w_0$ |
| First U-tube following the water-flask after the experiment .. .. | tare + 9·1488 |
| The same before the experiment .. | tare + 9·0970 |
| Hence, condensed steam . .. | 0·0518 = $w'$ |
| Second U-tube ($H_2SO_4$), after the experiment .. .. .. .. .. | tare + 2·6812 |
| The same, before .. .. .. .. | tare + 2·6805 |
| Hence, condensed steam . .. | 0·0007 = $w''$ |
| Third U-tube ($P_2O_5$), after .. .. | tare + 1·0499 |
| The same, before .. .. .. .. | tare + 1·0496 |
| Hence, condensed steam . .. | 0·0003 = $w'''$ |
| Hence, water-weight uncorrected = $w_0 + w' + w'' + w'''$ = | 19·2404 = W |
| Oxygen-weight uncor. = S = | 17·0926 |
| Hence, W − S (hydrogen) = .. | 2·1478 = *h* |

Hence $h : S = 0·12566$, whence (for O = 16) H = 1·00526.

In this experiment, for the first time, phosphoric anhydride tubes were used in conjunction with vitriol-tubes for drying the gas after leaving the copper-gauze tube and water receptacle, respectively. In all the preceding experiments, only two successive U-tubes with vitrioled pumice were used at either place. The above number ($w'''$) shows that, in Experiment 8 at least, the $P_2O_5$-tube might have been dispensed with.

In the following table, the headings of the columns refer to the *Proc. Phil. Soc. of Glasgow*; S stands for loss of weight suffered by the oxide of copper through its reduction to metal; $w_0$ for the weight of the liquid part of the water; $w$ for the water collected in the U-tubes attached to the water-receptacle; W for $w_0 + w$; H for the uncorrected atomic weight of hydrooen referred to O = 16.

*Table of Results.*

| Page .. | 68 | 70 | 72 | 74 | 76 | 78 |
|---|---|---|---|---|---|---|
| No. .. | (1) | (2) | (3) | (4) | (5) | (6) |
| S | 4·26195 | 6·71315 | 5·53935 | 10·03585 | 10·3715 | 10·5256 |
| $w_0$ | 4·7604 | 7·5038 | 6·20145 | 11·20945 | 11·6055 | 11·7933 |
| $w$ | 0·0376 | 0·0465 | 0·03575 | 0·0838 | 0·0673 | 0·0500 |
| W | 4·7980 | 7·55025 | 6·2372 | 11·29325 | 11·6728 | 11·8433 |
| H | 1·0061 | 0·9977 | 1·0080 | 1·0024 | 1·0037 | 1·0015 |

| Page | 80 | 82* | 84 | 86 | 88 | 90 | 92 |
|---|---|---|---|---|---|---|---|
| No. | (7) | 7.*a* | (8) | (9) | (10) | (11) | (12) |
| S | 10·4243 | 17·0926 | 18·5234 | 16·2367 | 15·4598 | 17·11485 | |
| $w_0$ | 11·6902 | 19·1876 | 20·78495 | 19·09975 | 17·3691 | 19·2266 | |
| $w$ | 0·0415 | 0·0528 | 0·0494 | 0·04065 | 0·03325 | 0·0365 | |
| W | 11·7317 | 19·2404 | 20·83435 | 19·1404 | 17·40235 | 19·2631 | |
| H | 1·0033 | 1·00526 | 0·9981 | 1·4307 | 1·00527 | 1·0041 | |

* A break-down.

*Summary.*
*Uncorrected Values for H Found.*
(No. 10 excluded.)

| No. | H. | No. | H. |
|---|---|---|---|
| 2 .. .. | 0·9977 .. .. | 12 .. .. | 1·0041 |
| 9 .. .. | 0·9981 .. .. | 11 .. .. | 1·0053 |
| 6 .. .. | 1·0015 .. .. | 8 .. .. | 1·0053 |
| 4 .. .. | 1·0024 .. .. | 1 .. .. | 1·0061 |
| 7 .. .. | 1·0033 .. .. | 3 .. .. | 1·0080 |
| 5 .. .. | 1·0037 | | |

Mean of the 11 values = 1·0032.
Probable error of a single determination = ±0·0021.
Probable error of the mean = ±0·00064.

The value W : S, even if taken in its empirical sense, is infected with an error which we had no idea of when the experiments were made; we refer to the presence of sulphurous acid in the hydrogen used. The quantity of this impurity per litre of gas used could not have been as great as in Dumas's case, because the two vitriol tubes

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* *Proceedings of the Philosophical Society of Glasgow.*

which followed our copper-gauze tube were very small compared with Dumas's. To form an idea of the probable magnitude of our error, we calculated the experiments tabulated under heading III., as so many determinations of the sulphurous acid per litre of total hydrogen used, taking every grm. of oxygen used in a synthesis as corresponding to 1·5 litres of hydrogen, measured moist over water at (we said) 15° and 748 m.m. dry gas pressure. The results varied from a very small negative quantity to 0·217 m.grm. as a maximum, the mean was 0·082 m.grm.* Assuming that the $SO_2$ in all the hydrogen used in the syntheses just tabulated amounted to 0·2 m.grm. per litre, we arrive at $H_2O : O = 1{\cdot}12506$, or $H = 1{\cdot}0005$ as corrected numbers. But 0·2 m.grm. per litre is more than the hydrogen can be assumed to have actually contained; hence the proper mode of interpreting the result is to say that the true value for W : S lies somewhere between 1·12506 and 1·1254, or that of H between 1·0005 and 1·0032. But, whichever value we choose, we must correct it for the air displaced by the copper and copper oxide, and for the air displaced by the water. Strictly speaking, each of our experiments should be corrected by itself; but, considering that our values for H oscillate between 0·9977 and 1·0080, it suffices to correct their mean, or to view the eleven experiments as, so to say, *one* experiment and correct its result.

In the eleven experiments which we allowed to vote, the total quantities of oxygen, water, and, by difference, hydrogen found, were as follow:—

| Oxygen. | Water. | Hydrogen. |
|---|---|---|
| 126·0624 | 141·8667 | 15·80435 |

Or, reducing to 1 grm. or 8 grms. of oxygen, respectively—

| | | |
|---|---|---|
| 1 | 1·125369 | 0·125369 |
| 8 | — | 1·00295 |

Leaving the sulphurous acid on one side for a moment, we must now reduce both the oxygen and the water to the vacuum.

*The Oxygen.*—Duplicate determinations of the specific gravities of the oxide of copper used, and of a specimen of the reduced copper obtained in an experiment gave the following results:—For the copper, 8·6959 and 8·7074—mean 8·7016; for the oxide, 6·1417 and 6·1420—mean 6·1418. In all the four determinations the temperature was 15°; yet we may, without committing a serious error, read the specific gravities as giving the weights of 1 c.c., and take the volume of 1 grm. of oxide of copper as = 0·16282 c.c., and the volume of 1 grm. of metallic copper as = 0·11492 c.c. The oxide of copper, however, was not pure CuO, but something between it and $Cu_2O$. The composition of the oxide, passing from experiment to experiment, was not by any means constant, but in one it was ascertained to correspond to the formula $O + 1{\cdot}0985\ Cu$. Assuming this formula and the above specific volumes to hold all round, we have, per 16 grms. of oxygen, for the volume of the oxide of copper, 14·850 c.c., for that of the metal 8·912 c.c., hence for the volume of the oxygen 5·938 c.c.; but this volume of air of 15° and 760 m.m. pressure weighs 5·938 × 1·2267 m.grms. Hence, for 1 grm. of oxygen the correction is = +0·4553 m.grm., and this added to the above 1 grm. gives 1·000455 grms. as the true weight of the oxygen. The 1·125 grms. of water displace 1·38 m.grms. of air, hence the true weight of the water = 1·12675 grms. Hence we have, for 1 grm. of oxygen, 0·12624 grm. of hydrogen, and for 8 grms. of oxygen, 1·0099 = H grm. Allowing 0·0014 for the sulphurous acid we have $H = 1{\cdot}0085 \pm 0{\cdot}0014$, on account of the *uncertainty* in this correction. But, unfortunately, this is not the whole of the uncertainty, for this reason: in the first instance, that the oxide of copper and the metallic copper must both be presumed to have contained absorbed gases which were weighed as so much oxide and metal respectively. Hence, when we came to carry out our second series of syntheses (which we projected as soon as we had discovered the reducing action of hydrogen on vitriol), we decided upon weighing our oxygen in the Dumas fashion, and did so (*vide infra*); and after the completion of that second series, it struck us that we might utilise the reduction-tube used in it for a summary determination of the *full* correction which the oxygen weights of the first series are liable to. For this purpose 115 grms. of the kind of oxide of copper which had been used in the second series were placed in the reduction-tube and subjected to exactly the same sequence of operations as would have been involved in a synthesis of water, with this difference only, that the oxide as well as the metal was weighed twice, namely, once in air against an open tare-tube, and once *in vacuo* against another, close, tare-tube. In the case of the metal the weighing in air came last, and it must be stated that the hydrogen-vacuum was *just undone and no more* by letting in dry air before the tube went to the balance. Two experiments were made in this manner, each with very nearly, but not exactly, 115 grms. of oxide. The results were as follow:—

*Weight of Oxygen Found.*

| | Experiment I. | Experiment II. |
|---|---|---|
| S, from weighings in air, uncorrected . .. .. .. | 21·5128 | 20·6520 grm. |
| $S_0$, by weighings *in vacuo* .. | 21·5322 | 20·6727 ,, |
| Hence, $S_0 - S =$ .. .. .. | 0·0194 | 0·0207 ,, |

—or, taking for each of the two quantities, the mean of the two experimental numbers, $S = 21{\cdot}0824$, $S_0 = 21{\cdot}10245$, $S_0 - S = 0{\cdot}02005$, whence—

$$\frac{S_0 - S}{S} = 0{\cdot}000950,$$

or 0·950 m.grm., for the weight of air displaced by 1 grm. of oxygen; and it is perhaps as well to note that the result would have been the same, practically, if the metal, previous to its first weighing, had been allowed to take up a few m.grms. of atmospheric oxygen. The above calculation, based on our determinations of the specific gravities of the oxide and metal, gave only 0·4553 m.grm.—a very considerable difference which cannot be explained by observational errors, nor by the admitted fact that the oxide used throughout the syntheses was not constant in its composition, and even that used for the specific gravity determination was not proved to have the composition $O + 1{\cdot}0985\ Cu$ adopted for the calculation of the correction for 1 grm. of oxygen, because we may well presume that the value of a given quantum of oxide of copper, which contains a small excess of metal (over and above that corresponding to CuO), is very nearly the same as if the surplus copper were present as a mere admixture of reduced metal. If we are right so far, then we have for the volume of $O + n\,Cu$ grm. of *this* kind of oxide the equation, $0{\cdot}11492\,n\,Cu + x = 0{\cdot}18926(n\,Cu + O)$, where $x$ stands for the volume of $O = 16$ grms. of oxygen. For the volume of 1 grm. of oxygen we have—

$$\frac{x}{16} = 0{\cdot}1628 + 0{\cdot}1893\,n,$$

and for the weight of air displaced by 1 grm. of oxygen at 15° and 760 m.m., the same × 1·2267 m.grm. Hence, by computation—

| For $n$ = | Weight of air displaced by 1 grm. of oxygen. |
|---|---|
| 1 | 0·4319 m.grm. |
| 1·0985 | 0·4553 ,, |
| 1·2585 | 0·4925 ,, |

We have reason to assume that 1·258 was about the maximum value which $n$ ever assumed in the course of

---

* The determinations here referred to have since been re-calculated, and suffered considerable corrections, yet we retain the result feeling sure that 0·2 m.grm. of $SO_2$ per litre is about as good a guess as it is possible to make.

our syntheses, and yet the corresponding air displacement (0·4925) is still far below the value 0·95 found by direct experiment. The difference, great as it is, must be charged against the absorbed gases.

The S of the syntheses, however, is liable to an additional correction, because in these the metallic copper, before being weighed, was exposed to a long-continued current of dry air, from which it must be presumed to have taken up, however small, a quantity of oxygen chemically. For a guess at the probable magnitude of this error, we re-heated the metal obtained in Experiment I. in hydrogen, and next re-weighed it *in vacuo*. We then allowed 4·5 litres of dry air to pass over it, and weighed it in an air-vacuum. As a last step, the vacuum was undone by admitting hydrogen, this hydrogen pumped out, and the metal weighed in a hydrogen vacuum. We found, for the *weight of the tube and contents*—

| | |
|---|---|
| (1) Pure copper in hydrogen vacuum . .. .. .. | tare + 8·0012 grms. |
| (2) Slightly oxidised copper in an air vacuum.. .. | tare + 8·1056 ,, |
| (3) The same in a hydrogen vacuum.. .. .. .. | tare + 8·0153 ,, |

From (1) and the mean of (2) and (3) we have weight of oxygen absorbed as $Cu_2O = 14·25$ m.grm.

To utilise the present experiment as a means for correcting the oxygen weights found in the syntheses, let us assume that the metallic copper obtained in the first test experiment, after having been weighed (as pure Cu) *in vacuo*, had been allowed to combine with 14·25 m.grm. of oxygen before being weighed in air. The uncorrected oxygen weight then would have been 21·5128 − 0·01425 grm., but the true value $S_0$ would have been the same as reported. Hence (substituting the means of the two values $S_0$ and S for those found in Experiment I.), we have—

Faulty oxygen weight, S = .. 21·06815 grms.
True oxygen weight, $S_0$ = . .. 21·10245 ,,
Hence, $S_0 - S$ = .. .. .. .. .. 34·30 m.grms.

—and, consequently, for the correction per S = 1 grm. the value + 1·6281 m.grm. From our notes concerning the volumes of air which, in the syntheses, were passed over the metal to be weighed, we conclude that in these the weight of oxygen taken up by unit of copper was less than it was in the test-experiment; we, therefore, now proceed to correct the data afforded by the sum of the syntheses on the basis of three successive assumptions.

I.—*The oxygen taken up amounted to* 14·25 *m.grm. per* S = 21·068 *grm.*

| | Oxygen. | Water. | Hydrogen. |
|---|---|---|---|
| Uncor. numbers, as above .. .. .. | 1 | 1·125369 | |
| Corrections .. .. | +0·001628 | +0·001382 | |
| Corrected numbers | 1·001628 | 1·126751 | 0·125123 |
| Or reducing to $S_0 = 1$, | 1 | — | 0·124920 |

whence $H_0 = 0·99936$.

II.—*The oxygen taken up amounted to* 7·0 *m.grm. per* S = 21·068 *grm.*

| | Oxygen. | Hydrogen. |
|---|---|---|
| Corrected numbers .. .. | 1 | 0·125309 |

whence $H_0 = 1·00247$.

III.—*There was no oxygen taken up at all.*

| | Oxygen. | Hydrogen. |
|---|---|---|
| Corrected numbers .. .. | 1 | 0·125681 |

whence $H_0 = 1·00545$.

If our guess at the correction for the sulphurous acid be correct, each of the three numbers for $H_0$ must be diminished by 0·0014, but *this* correction, under the circumstances, is not worth applying.

(To be continued).

# NOTE ON THE DETECTION OF BROMINE, CHLORINE, AND IODINE IN THE SAME MIXTURE.

By F. P. DUNNINGTON.

In the article of Mr. Lyman F. Kebler (*Jour. Anal. App. Chem.*, vi., 569) upon this subject, he gives a *resumé* of the methods employed, and alludes to the necessity of employing soluble haloid salts for the most satisfactory of the processes.

For some years I have with satisfaction used a method which I have recently put in print in the second edition of Professor F. P. Venable's "Qualitative Analysis," 1892, p. 46. It is as follows:—From a solution acidified with nitric acid precipitate the silver salts of these acids with silver nitrate solution; having filtered off and washed this precipitate, treat it in a test glass with a few drops of very dilute sulphuric acid and a bit of zinc; when the dark spongy mass of metallic silver is formed, pour off the solution of the zinc salts and examine it for iodide, bromide, and chloride by the method of Professor Edward Hart.—*Jour. Anal. App. Chem.*, vol. vi., p. 611.

**A Novel Theory of Dyeing.**—It is well known that two theories have been maintained in explanation of the process of dyeing. According to the one—the so-called mechanical view—the process is a simple absorption, similar to that by which animal charcoal takes up gases and liquids and retains them in its pores. The other theory, traces the phenomena of dyeing to definite combinations. Neither of the above theories is perfectly satisfactory. In consequence, M. Witt has put forward a theory in which he assimilates tinctorial operations to the phenomena of solution, or, in other words, to combination in indefinite proportions. He maintains that the colouring-matter is dissolved in the fibre, which becomes dyed only if its affinity for the colouring-matter is greater than that of the previous solvent. Thus, wool is dyed by magenta dissolved in water, but is not dyed if the colour is dissolved in pure alcohol. If the solvent powers of the fibre and of the water are approximately equal, there is established a kind of equilibrium, and the dye-bath does not become completely exhausted. If the solvent power of the fibre is less than that of the water there is no dyeing. In this case the solvent power of the water may be decreased by adding sodium chloride or sulphate, &c. Or the solvent power of the fibre may be heightened, *e.g.*, by chloring wool, or by depositing sulphur upon it, or by mercerising cotton.—E. Noelting, *Revue des Sciences.*

**On Calcium Tartrate Extracted from the Dregs of Distilleries, its Determination and its Refining.**—Ch. Ordonneau.—The author took up the idea some years ago to extract the tartaric acid from the residues of wine-distilleries in the form of calcium tartrate. He infers, on statistical evidence, that if these residues had been utilised in the Charentes in, *e.g.*, 1875, tartaric acid could have been obtained sufficient for the demand of the whole of Europe. M. Ordonneau gives a method for the determination of tartaric acid more accurate than the Goldemberg process. This process will be inserted in full.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 3.

# THE DETECTION AND DETERMINATION OF ARSENIC.*

By JOH. THIELE.

(Continued from p. 126).

### 3. *On the Use of Platinised Zinc in the Marsh Apparatus.*

In testing for arsenic with the Marsh apparatus it is universally customary to expedite the solution of the zinc by adding a few drops of solution of platinum. Thiele, however, makes the observation that this addition of platinum diminishes the sensitiveness of the reaction—perhaps in consequence of the formation of platinum arsenide—so that small quantities of arsenic may quite escape recognition. Thus, with platinised zinc, using hydrochloric acid as generating liquid, 0·05 m.grm. arsenious acid gave a moderately strong mirror, but decidedly fainter than with non-platinised zinc. If only 0·02 m.grm. of arsenious was present, the reaction failed entirely in nine out of eleven trials; whilst the same quantity of arsenic without platinum always gave distinct mirrors. Quite identical results were obtained with an addition of platinum and dilute sulphuric acid. The sensitiveness of the reaction cannot be here determined, as the very pure zinc employed was substantially insoluble in the absence of platinum.

Zinc may be platinised by immersion in a 10 per cent solution of platinum chloride and subsequent rinsing, or by adding 3 to 4 drops of this solution to the contents of the apparatus. Before adding the arsenical solution or substance it is necessary to wait until the platinum has been completely deposited.

### 4. *On the Precipitation of Arsenic Acid with Hydrogen Sulphide.*

Thiele has investigated this method, and confirms essentially the results of Brauner and F. Tomicek, of Le Roy W. McCay, and R. Bunsen.

Arsenic acid is precipitated as arsen pentasulphide from an acidified hot solution of hydrogen sulphide, whilst if the current of gas is slow a mixture of pentasulphide and trisulphide is thrown down.

If, on the other hand, a solution of arsenic acid in concentrated hydrochloric acid is treated in the cold with a rapid current of sulphuretted hydrogen we obtain a mixture of pentasulphide with sulphur and trisulphide.

According to the author's experiments arsenic acid is thrown down from a hot hydrochloric solution partially as sulphide, even with a rapid current of hydrogen sulphide if the gas is diluted.

J. Mayrhofer has made the observation that arsenic acid is reduced to arsenious acid by highly concentrated hydrochloric acid. According to an experiment of the author's no appreciable reduction of the arsenic acid takes place at the ordinary temperature if it is dissolved in hydrochloric acid of specific gravity 1·15.

Concerning the determination of arsenic by its quantitative volatilisation as arsenic hydride, numerous experiments have been made which so far have not led to any satisfactory results. F. W. Schmidt (*Zeit. f. Anorg. Chemie*) has resumed the experiments, having observed that the arsenic in commercial zinc powder may be completely volatilised as arsenic hydride by treatment with hydrochloric acid.

In the first place the proportion of arsenic in the zinc powder was accurately determined as follows:—

Ten grms. zinc powder were cautiously dissolved in concentrated nitric acid, which was then expelled by evaporation with concentrated hydrochloric acid on the water-bath. After reducing the arsenic acid with ferrous chloride (according to E. Fischer), the arsenic was distilled over with hydrochloric acid and determined in the distillate both gravimetrically as trisulphide, and in a second experiment volumetrically with iodine solution. The quantity of arsenic was found by both methods as 0·04 per cent.

For determining the arsenic by volatilisation as hydride the following apparatus was employed. It consisted of a globular funnel, holding 200 c.c., fitted with a tube funnel and a gas delivery pipe leading to three absorbent vessels, each of 100 c.c. capacity. Caoutchouc stoppers were used. The gas delivery tube does not project into the flask, but its aperture is in one plane with the lower surface of the stopper; the delivery tubes have a pointed end.

The round flask is placed on a water-bath in order to assist the reaction by heat. The distance of the first absorbent vessel from the globular flask was at least 20 c.m., so that the liquid is not heated in the absorbent vessel, which might easily occasion the formation of arsenic acid. The first absorbent vessel was half filled with solution of silver nitrate of the strength 1 : 50; the second with silver nitrate at 1 : 10; and the third contained bromine-hydrochloric acid.

Ten grms. of commercial zinc powder were then weighed into the globular flask. After the substance had been moistened with water, the apparatus was put together, hydrochloric acid was gradually introduced through the dropping tube—1 vol. concentrated acid to 1 vol. water—and allowed to flow down to the zinc powder. The gas evolved at once deposited black metallic silver in the first flask. When the escape of gas began to grow sluggish the flame was lighted under the water-bath. When the zinc powder was completely dissolved a slow current of hydrogen washed in silver nitrate (1 : 10), and consequently free from arsenic, was introduced (keeping the globular flask heated) for half an hour in order that the last traces of arsenic hydride may be removed from the flask. The contents of the third absorbent vessel and of the globular flask were found perfectly free from arsenic hydride. Hence all the arsenic had escaped in combination with hydrogen, and the transformation of the arsenic hydride with the silver solution was completed in the second absorbent flask, so that the third contained no trace of arsenic. The excess of silver was removed from the contents of the first and second absorbent vessels by means of a solution of sodium chloride, and the filtrate from the silver chloride was titrated for As by means of decinormal solution of iodine after the addition of sodium hydrocarbonate. In this manner there was found a proportion of arsenic in the zinc powder of 0·04 per cent, which agrees with the result of the gravimetric method.

The complete volatilisation of the arsenic from the zinc powder in the state of arsenic hydride depends probably on the circumstance that the arsenic in the zinc powder is present as zinc arsenide or in a very finely-divided metallic condition, which especially favours the quantitative conversion of arsenic into its hydrogen compound. A quantitative volatilisation of the arsenic must therefore be possible in other cases if the arsenic could be brought into a state analogous to zinc arsenide or into a very fine state of metallic division.

(To be continued).

**Certain Molecular Compounds of the Amines.**—W. Rednew.—According to the author, a close examination of these molecular compounds may throw a clearer light on the difference between these and ordinary atomic compounds. The molecular compounds are distinguished from many ordinary compounds by the circumstance that in the latter the atomic compounds originally present in their components remain unaltered. Hence it is plain that, *e.g.*, ammonium chloride cannot be regarded as a molecular compound, whilst certain compounds of ammonia with metallic salts are probably molecular compounds.—*Journ. Prak. Chemie*, xlvi., Part 5.

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* From the *Zeit. Anal. Chemie.*

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, March 2nd, 1893.*

Dr. J. H. Gladstone, F.R.S., Vice-President, in the Chair.

Messrs. T. K. Rose, K. K. Kacker, and C. M. Luxmoore were formally admitted Fellows of the Society.

It was announced that the following additions to the by-laws proposed by the Council would be presented for consideration at the coming General Meeting.

1.—In By-Law XI., after the words "The ordinary Scientific Meetings of the Societies shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only," to add the words "and also at Easter, when, if the Council see fit, there shall also be only one meeting in the month."

2.—In Bye-Law XIII. to add the following paragraph:—"At all General Meetings of the Society, whether annual or extraordinary, no motion of a proposal to alter the by-laws shall be considered of which due notice has not been given, at least 14 days previously, either at an ordinary Scientific Meeting, or through the agency of the *Proceedings*, or by means of a printed notice addressed to all the resident Fellows."

Attention was directed to the following resolutions passed at a meeting held on March 1st, 1893, at the Royal Agricultural Society's rooms, H.R.H. the Prince of Wales, K.G., in the Chair:—

"That, having regard to the great national importance of the series of experiments which have been carried on at Rothamsted during the last 50 years, it is desirable that some public recognition should be made of the invaluable services thus rendered to agriculture by Sir John Lawes, and also by Dr. Gilbert, who has been associated with the experiments during the whole period.

"That, with this object, subscriptions, to be limited to two guineas, be invited from all interested in agriculture, whether scientific or practical.

"That, in the opinion of this meeting, the testimonial might advantageously take the form of (1) a granite memorial, with a suitable inscription, to be erected at the head of the field where the experiments have taken place; (2) addresses to Sir John Lawes and Dr. Gilbert, accompanied (if funds permit) by a commemorative piece of plate."

Ordinary certificates were read for the first time in favour of Messrs. John Charles Burnham, 179, Griffin Road, Plumstead; James Cameron, Nobel's Explosive Co., Polmont Station, A.B.; Henry Williamson Dixon, 258, Hunslet Road, Leeds; Thomas Edwards, Brewery House, Rhymney; Hedley Gordon Jones, 15, Rectory Place, Woolwich.

Of the following papers, those marked * were read:—

*121. "*The Magnetic Rotation and Refractive Power of Ethylene Oxide.*" By W. H. Perkin, Ph.D., F.R.S.

The following values are recorded in the paper:—

$d$ 4°/4° = 0·8989; $d$ 7°/4° = 0·88654; $d$ 7°/7° = 0·8867; $d$ 10°/10° = 0·8824.

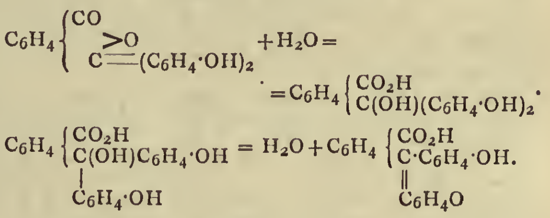
Molecular magnetic rotation at 8° = 1·935.
Molecular refraction at 7°, A = 17·680.
Dispersion, G − A = 0·5494.

It is pointed out that the magnetic rotation is most remarkably low, and the refractive power also below the calculated value (A = 18).

*122. "*The Origin of Colour (including Fluorescence). VII. The Phthaleins and Fluoresceins.*" By Henry E. Armstrong.

In the first of these communications on the origin of colour (*Proc. Chem. Soc.*, 1888, No. 4, p. 27), exception was taken to the formulæ assigned to phenolphthalein and its congeners. Although the exhibition of colour by these substances could not be accounted for by the formulæ ascribed to them, the data then available were insufficient to permit of more satisfactory formulæ being devised. The subsequent discovery of the rhodamines strengthened this conviction, and the intention to make these the subject of experimental study as soon as an opportunity occurred has long been kept in mind; fortunately this is no longer necessary, the technical value of these substances having led to their further investigation in various works laboratories, with the result that they have been shown, as was anticipated, to exhibit properties proving that they also are quinonoid compounds.

The *Chemiker Zeitung*, No. 104, December 28, 1892, contains an account of a communication made to the Heidelberg Chemical Society on December 16, by Prof. Bernthsen, who points out that the rhodamines afford true ethereal salts when subjected to the conjoint action of alcohol and chlorhydric acid: in other words, that they afford carboxy-compounds and not lactone derivatives. After directing attention to other evidence in favour of the view that the colours of this class are members of the triphenylmethane group, he points out, in so many words, that the characteristic development of colour on adding alkali to phenolphthalein is, in all probability, due to the fact that the colourless lactone phenolphthalein is thereby hydrolysed and converted into a quinolic compound, which suffers dehydration, affording a coloured quinonoid compound:—



$$C_6H_4\left\{\begin{array}{l}CO\\ \quad >O\\ C{=\!=}(C_6H_4{\cdot}OH)_2\end{array}\right. + H_2O = \\ = C_6H_4\left\{\begin{array}{l}CO_2H\\ C(OH)(C_6H_4{\cdot}OH)_2\end{array}\right.$$

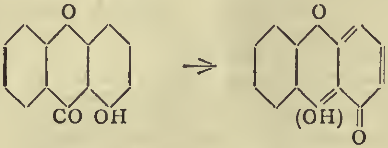
$$C_6H_4\left\{\begin{array}{l}CO_2H\\ C(OH)C_6H_4{\cdot}OH\\ |\\ C_6H_4{\cdot}OH\end{array}\right. = H_2O + C_6H_4\left\{\begin{array}{l}CO_2H\\ C{\cdot}C_6H_4{\cdot}OH.\\ \|\\ C_6H_4O\end{array}\right.$$

In a more recent paper (*Berichte*, 1893, 172), Friedländer—who does not appear to be aware of Bernthsen's communication, has stated that phenolphthalein and hydroxylamine readily interact in an alkaline solution and form a hydroxime; this and other evidence he mentions leads him to express the opinion that in their coloured state phenolphthalein and the allied phthaleins which behave similarly in presence of alkali are all *quinonoid* compounds.

But, as so frequently happens at the present day, the patent literature contains statements which anticipate the views of Bernthsen and Friedländer, *e.g.*, a description being given of the formation of ethereal salts of rhodamines by the action of alcohol and chlorhydric acid in the French patent specification No. 224603, of the "Farbenfabriken vormals Friedr. Bayer und Co." (Elberfeld), dated September 28, 1892. It is pointed out in this specification that the rhodamines are to be regarded as carboxylic compounds, and the absence from the ethereal salts of the property which the rhodamines exhibit of forming salts and lakes is referred to as confirmatory of this view.

Friedländer is led to regard the fluoresceins as perhaps different from the phthaleins, as he was unable to obtain hydroximes from them, and speaks of their colour as conditioned by their xanthone-like structure. There appears to be no reason, however, why a distinction should be drawn between the intensely fluorescent rhodamines and the analogous oxygenated compounds—the fluoresceins.

Even regarding them as xanthone derivatives, the appearance of colour in these latter is, it can scarcely be doubted, consequent on the occurrence of isodynamic change (*cf. Proc. Chem. Soc.*, 1892, 103).



Colourless. Coloured.

The problem, therefore, remains practically the same; nevertheless, there can be little doubt that the phthalein-fluorescein group still offers interesting matter requiring further study.

Perhaps the point of chief interest claiming attention is the extraordinary ease with which the hydrolysis of the lactone is effected in the case of phenolphthalein, as evidenced by the fact that it is among the most sensitive of the known indicators of alkali: in contemplating the changes which may attend the dissolution of substances by water, such facts are undoubtedly of high importance. Perhaps the change is less a consequence of the instability of the lactone ring, and is mainly conditioned by the hydroxyl present in the para position relatively to the carbon atom to which the phenolic radicles are attached—it is conceivable that a hydrated metallic derivative of the phenol is initially produced, and that the metal and water necessary to effect the hydrolytic change are thus brought into the intramolecular sphere of interaction. From this point of view it would be interesting to determine the degrees of readiness with which phthalid and its various derivatives undergo hydrolysis. It is also worth noticing that, according to Bernthsen, the anhydrous rhodamine base forms a colourless solution in benzene, and may be obtained in large colourless crystals, while its solution in water is coloured, and it forms an intensely coloured pentahydrate.

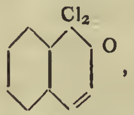
The recognition of the quinonoid character of such eminently fluorescent substances as the fluoresceins and rhodamines may be claimed as a most important argument on behalf of the view that fluorescence is a form of colour: indeed that, taken in conjunction with other facts, it goes far towards justifying the contention that all quinonoid derivatives would be visibly fluorescent, were it not that, as in the case of certain quinine salts, as Hartley has pointed out, the rays which are the cause of the fluorescence sometimes become absorbed in the solution.

### *123. "*The Origin of Colour.* VIII. *The Limitation of Colour to Truly Quinonoid Compounds. Change of Colour as Indicative of Change of Structure, as in the case of Alizarin.*" By Henry E. Armstrong.

A quinonoid compound may be defined as a *hexaphene*, *i.e.*, an unsaturated cycloid composed of six "elements" (*cf. Proc. Chem. Soc.*, 1892, 129), two "elements" of which are C⊃R″ groups in either para- or ortho-positions.

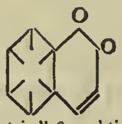
Coloured substances generally appear to fall within this definition, as there do not appear to be any established cases of the existence of coloured substances (*a*) containing a single C⊃R″ group, or (*b*) in which two such groups are present in a cyclane or saturated ring, or (*c*) in which the cycloid contains any other number of elements than six. The succinosuccinic derivatives, &c., are but apparent exceptions to *b*, as those which are coloured may be regarded as isodynamic forms of the saturated compounds, Diacetyl and dibenzoyl (benzil) may be mentioned as exceptions to the general definition, but for this very reason it appears likely that they will eventually be obtained colourless; it is easy to account or the appearance of colour in diacetyl, as it undergoes condensation with extreme facility, yielding dimethylquinone (paraxyloquinone). an intensely yellow substance. Such a change is not likely to occur in the case of benzil, but this compound is so faintly yellow that the colour may well be due to impurity.

Some of the keto-chlorides described by Zincke appear to be exceptions to *a*, *e.g.*, the compound—

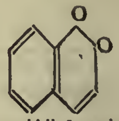


prepared by chlorinating betanaphthol, the colour of which is a yellow of considerable intensity, and there is no reason to suppose that this is not characteristic of the pure compound. It is not improbable, however, that the group $CCl_2$ in this and similar substances may be the true equivalent of a C⊃R″ group. In an article on "The Determination of the Constitution of Carbon Compounds from Thermochemical Data," published in the *Phil. Mag.*, in February, 1887, summarising and briefly discussing the results described in the fourth volume of J. Thomsen's *Thermochemische Untersuchungen*, it was suggested that the greater development of heat which attends the formation of symmetrical dichloro-derivatives may be due to the partial neutralisation of the (residual) affinity of the one chlorine atom by the other: in other words, that chlorine atoms are possessed of the power of directly entering into association while combined with another atom, in which case 2Cl would be the equivalent of R″.

As the presence of two ortho- or para-carbonyl groups in a saturated ring apparently does not condition colour, it would seem that the two C⊃R″ groups are concerned *together with* the "ethenoid linkages" in the unsaturated ring in the production of colour; hence, the fact that compounds such as the naphthaquinones and the keto-chloride before referred to are coloured is of importance, as evidence that *perhaps* a single ethenoid linkage in the ring is sufficient, and that it is not necessary that there should be two such, symmetrically situated with reference to the two C⊃R″ groups as in the benzoquinones; this, however, is on the assumption that the naphthaquinones are derivatives of *centric* and not of *ethenoid* benzene, hence the perhaps; the importance of this consideration will be more clearly realised after reference to the arguments made use of in the two following notes:—

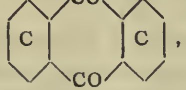


"Centric" β-naphthaquinone.



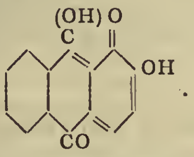
"Ethenoid" β-naphthaquinone.

Anthraquinone—which, it may be remarked, has scarcely any of the properties of a true quinone—may be referred to in this connection: if represented as a derivative of *centric* benzene, thus—



the median group would appear to be saturated; yet, as anthraquinone may be regarded as formed by the superposition of benzene and quinone, it would seem that the median group is still possessed of quinonoid characteristics; unless it be that the effect of the two CO groups is supplemented by that of the two symmetrically placed centric cycloids.

It would seem appropriate to here direct attention to the colour of alizarin in comparison with that of anthraquinone. The colour of paraquinones and their derivatives, in all cases in which the structure appears to be in no way open to question, is uniformly yellow; and red is characteristic of orthoquinones. How comes it then that alizarin is red? The conventional formula is not in accord with this fact, but the colour may be accounted for by regarding alizarin as an isodynamic form of dihydroxyanthraquinone, *e.g.*,



On this assumption there is no difficulty in understanding why the monhydroxyanthraquinones are of no use as dye-stuffs; and why the introduction of two contiguous hydroxyls into anthraquinone is of such importance; furthermore, it is to be expected that a monethoxy-derivative prepared from alizarin if it contained an $\alpha$-ethoxy-group would resemble anthraquinone while one containing a $\beta$ ethoxy-group would more nearly resemble alizarin in colour: and, as a matter of fact, two such compounds have been described, one of which is yellow and the other red.

In like manner it may be suggested as probable that the chloranilates are not derivatives of paraquinone, and that their formation involves the occurrence of isodynamic change, thus:—

The arguments advanced in proof of their paraquinonoid nature do not appear to be in any way conclusive. Lastly, reference may be made to the *phenoquinones* and *quinhydrones*: it is difficult to regard these as being other than members of that ill-understood and vaguely-defined class of substances termed molecular compounds. If so, the changes in the colour of quinones involved in their formation may arise from the weighting of the C⊃R″ groups by the attachment thereto of the phenol.

(To be continued).

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## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 10, March 6, 1893.

**Analysis of the Ash of the Diamond.**—Henri Moissan.—All the samples of bort and of diamonds from the Cape which we have examined contained iron which formed the chief part of the ash. It has also been found in the ash of carbonado and of Brazilian diamonds, except a variety of bort of a green colour, which is totally free from it. In all the samples silicon has been detected, and in most of them calcium.

**Certain New Properties of the Diamond.**—Henri Moissan.—The temperature of the combustion of the diamond varies with different specimens; it fluctuates between 760° and 875°. In general the harder a diamond the higher is its temperature of combustion. If a diamond resists at 1200° chlorine, hydrofluoric acid, and the action of different salts, it is, on the contrary, easily attacked at this temperature by the alkaline carbonates, and this decomposition in a gaseous form has enabled us to prove that the specimen studied contained neither hydrogen nor hydrocarbons.

**New Derivatives of Phenolphthalein and Fluoresceine.**—A. Haller and A. Guyot.—This memoir is not adapted for useful abstraction.

**Election of a Foreign Associate vice Sir Richard Owen.**—Sir Joseph Lister was elected by a large majority. He received 46 votes as against 6 given to Baron Nordenskiöld and 5 to Mr. Newcomb.

**Industrial Preparation of Alumina.**—A. Ditte.—Bauxite is treated with caustic soda, the aluminate obtained is mixed with a small quantity of crystalline alumina, and the solution of aluminate is treated in the cold with a current of carbonic acid, which gives rise to a precipitate of aluminium hydroxide easily washed. At the end of some hours there remains merely a small quantity of alumina in solution.

**The Isomerism of the Amidobenzoic Acids.**—Oechsner de Coninck.—The author has studied the solubility of the three acids in different media; in the hydracids, in certain oxacids, both mineral and organic, and in certain media having an alkaline reaction.

**Dimorphism of Dimethylamine Chloroplatinate.**—Le Bel.—It appears that among the chloroplatinates of the amines, the dimethylamine compound forms various double salts, and, in particular, that it unites in equal molecules to that of dipropylamine, forming a double salt remarkablywell crystallised. A mixture of the dimethyl- and diethylamine-chloroplatinates merely furnishes the compounds of dimethylamine and diisobutylamine. The power of forming double salts seems therefore restricted to very special terms.

**On Inuline and Two New Proximate Principles: Pseudoinuline and Inulenine.**—C. Tanret.—The composition of inuline is $C_{72}H_{62}O_{62}$. It is very soluble in hot water, but requires more than 10,000 parts of cold water for solution. It is also readily soluble in hot weak alcohol. Its aqueous solutions are very limpid and not opalescent like those of leucogen, to which they have been erroneously compared. Baryta-water dissolves inuline at first, but a further addition precipitates the compound $C_{72}H_{62}O_{62}6BaO$. This reaction is very sensitive, and is given very distinctly by a solution of inuline at 1·600th. Pseudoinuline has the composition $C_{192}H_{102}O_{102}$. Its barium compound is more soluble than that of inuline, whence a solution of pseudoinuline at less than 3 per cent is not precipitated by baryta-water. Pseudoinuline is not precipitated by lead subacetate without an addition of ammonia. Inulenine has the composition $C_{120}H_{104}O_{104}$. Cold baryta-water dissolves inulenine without the formation of a precipitate by an excess, but it is thrown down by luke warm concentrated solution of baryta.

**Absorbent Action of Cotton on Dilute Solutions of Mercuric Chloride.**—Léo Vignon.—The author has formerly shown (*Comptes Rendus*, Feb. 10 and April 28, 1890) that animal fibres have definite chemical functions, basic and acid, whilst vegetable fibres display feeble chemical functions and especially no basic functions. Cotton must therefore be considered as a feeble acid, the chemical function of which becomes more intense as the proportion of oxycellulose increases. The author has now extended these ideas to the absorbent action of cotton on dilute solutions of corrosive sublimate. The mercury chloride in which the cotton has been steeped is impoverished in mercury. The cotton combines with mercuric oxide, whilst it is merely impregnated with hydrochloric acid without entering into combination. The author intends to determine if the mercury is fixed upon the cellulose as oxide or as oxychloride, and if a part of the mercury thus fixed passes into the state of mercurous chloride.

**Remarkable Resistance of Goats to the Effects of Morphine.**—L. Guinard.—Whilst 0·0003 grm. per kilo. of live weight narcotises a man, a proportion one thousand times greater is easily endured by goats.

**Perfumes of the Orchids.**—Eugène Mesnard.—One and the same flower of an orchid emits decidedly different odours, according as it is observed in the morning or at night, as it has been exposed to the sun or kept in the shade, as it has been gathered when freshly opened or is fading. A very remarkable periodicity has even been observed in the development of the perfume of certain orchids. M. Mesnard admits, however, that he cannot at present submit any hypothesis in explanation of this phenomenon.

### *Journal fur Praktische Chemie.*

New Series, Vol. xlvi., Parts 5, 6, and 7.

**Researches on Alloisomerism.**—Arthur Michael.—Already inserted.

**On the Methylnaphthalines.**—Gustav Wendt.—This memoir is chiefly a critique on a paper in the Berlin *Berichte* (xxiv., 3918) by Prof. H. Wichelhaus.

**The Double Haloid Compounds of Gold.**—Emil Petersen.—On the action of a rapid current of chlorine upon finely divided gold without the aid of external heat, but with retention of the heat of the reaction, there is chiefly formation of $Au_2Cl_4$, with smaller quantities of a trichloride. $Au_2Cl_4$, on treatment with refrigerated alcohol, gives off to the latter trichloride, whilst there remains monochloride, which latter, on the prolonged action of alcohol, is partially resolved into gold and trichloride. Krüss and Schmidt propose to eliminate $Au_2Cl_4$ and the corresponding bromine compound from the series of gold compounds. The author, however, insists on their retention as true chemical compounds chiefly on thermochemical evidence.

**Researches from the Laboratory of the University of Freiburg.**—Ad. Claus.—The author criticises the recent treatise of Grimaux (*Comptes Rendus*) on the quinine iodomethylates, and discusses the relations of quinine, quinidine, cinchonin, and cinchonidine.

**Condensation of β-Diketones with Urea and Thiourea.**—P. Evans.—A preliminary communication.

## MISCELLANEOUS.

**Royal Institution.**—The following are the Lecture Arrangements after Easter:—John Macdonell, three lectures on "Symbolism in Ceremonies, Customs, and Art"; Professor R. K. Douglas, three lectures on "Modern Society in China"; E. L. S. Horsburg, three lectures on "The Waterloo Campaign"; Professor Dewar, five lectures on "The Atmosphere"; R. Bowdler Sharpe, four lectures on "The Geographical Distribution of Birds"; James Swinburne, three lectures on "Some Applications of Electricity to Chemistry" (the Tyndall Lectures); Henry Craik, C.B., three lectures on I. "Johnson and Milton," II. "Johnson and Swift," III. "Johnson and Wesley"; Dr. A. C. Mackenzie, three lectures on "Falstaff," a Lyric Comedy, by Boito and Verdi (with Musical Illustrations, by kind permission of the composer and publishers, Messrs. Ricordi, specially granted for these lectures). The Friday Evening Meetings will be resumed on April 14th, when a Discourse will be given by Sir William H. Flower, K.C.B., on "Seals"; succeeding Discourses will probably be given by Professor A. B. W. Kennedy, Professor Francis Gotch, Mr. Shelford Bidwell, The Right Hon. Lord Kelvin, Mr. Alfred Austin, Mr. Beerbohm Tree, Professor Osborne Reynolds, Professor T. E. Thorpe, and other gentlemen.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Testing for Cotton in Woollen Goods.**—(Reply to F. S. C.)—The usual and best reagent is caustic potash or soda, which dissolves the wool and leaves the cotton. Use a solution of 1·02 sp. gr.; boil for 15 minutes, wash, and dry carefully. For details see Chemical News, vol. xliv., p. 262, and vol. l., p. 123.—P. D. R.

## MEETINGS FOR THE WEEK.

Monday, 27th.—Medical, 8.30.
—— Chemical, 8. (Annual Meeting). President's Address. Election of Office Bearers and Council.
Tuesday, 28th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
Wednesday, 22nd.—British Astronomical Association, 5.

Errata.—In the Report of the Physical Society, p. 131, col. 2, line 25 from top, *for* "reserved" *read* "reversed." Line 52, *for* "optical" *read* "special. P. 132, col. 1, line 17 from bottom, *for* "size" *read* "sine."

THE CHEMICAL NEWS.

Vol. LXVII., No. 1740.

## ON THE ORIGIN OF COLOUR.

### IV. Vibrations. Break-Ethers. Oxygen.

By WILLIAM ACKROYD.

(Concluded from p. 111).

No cause has been assigned that I am aware of for what Sorby has termed "the band-raising power" of solvents (*Proc. Roy. Soc.*, xxi., 1873, p. 443). The theory of vibrations has been applied by Carnelley (*Phil. Mag.*, 1884, pp. 139 and 140), and previously by Houston and Thompson (Chemical News, xxiv., p. 188), to explain the colour changes of solids and liquids. In my paper on "Metachromatism" (Chemical News, xxxiv., p. 77), I have attempted to show that "atomic potentiality" is the only necessary concomitant of colour change,—a view which brings the phenomena within the bounds of allotropy and isomerism. Now, as then, I am persuaded that writers have not acquainted themselves with the infinitesimal nature of the vibrations they have called to their aid in attempting to explain colour change. The following example will illustrate my contention.

Silver iodide above its point of maximum density, 116° C., expands upon being heated with the normal order of colour change; thus from yellow at 116° it becomes gradually darker until at 180° it is orange-red; at 412° a dark brick-red, and at 450° a dark red liquid. Now what increase in amplitude of molecular vibration is there in changing, say, from yellow AgI at 116° C. to the red salt at 216° C? Rodwell gives good reasons for assuming that a volume of 1·00000 at 116° C. becomes a volume of 1·01455238 at 450° C. (*Proc. Roy. Soc.*, No. 157, 1875). Therefore a row of AgI molecules, 1 c.m. long at 116°, will have increased to 1·001452 c.m. at 216° C. In this row there will be from one hundred millions to two thousand million molecules according to Lord Kelvin's estimate. Hence it follows that one of these molecules through a range of 100° during the change of colour from yellow to red is not disturbed from its relative position with regard to the others, in round numbers, more than a thousandth of a tenth-metre, or, say, five-millionths of the length of a wave of light. While not denying that vibrations of this order of magnitude may have a marked effect in the absorption of light, and also be the cause of fluorescence in bodies exhibiting this phenomenon, I am disposed to look for the origin of colour to the more proximate cause of molecular aggregates.

In the length of an ether-wave, a thousand molecules can be ranged, and I shall here advance the view that aggregates of thousands of these molecules are required to dissipate the ether-waves in producing selective absorption like masses of rock breaking up the sea-waves. It may indeed be that just as the stillness of a Norwegian fjord as compared with the turbulence of the outer ocean is produced by the natural break-waters of the outlying islands, so the etherial tranquillity within a coloured body, denoted by absorption of light, may be due to these natural *break-ethers* of molecular aggregates.

The nearest approach to this conception would be that of a liquid with minute particles in suspension and exhibiting phenomena such as I find a solution of sulphuretted hydrogen exhibits. When it is first prepared, and for a few days afterwards, it presents the following appearances when viewed by transmitted diffused daylight.

| | |
|---|---|
| First day .. .. | Yellow. |
| Second day . .. | Blue with yellowish reflection. |
| Fourth day . .. | Sea-green with pinkish reflection. |

And as the particles settle it is finally without colour. This phenomenon, with occasional variations in the nature and order of colour change, is best seen with the soft moorland waters in use here; with harder well-waters the deposition of suspended particles is more rapid and the colour effects not so marked. We may perhaps regard the first effect as being due to the action of particles of three different orders of size on the light; as one of these subsides the next effect is blue, and finally, as none but the finest particles are left, the liquid appears sea-green. If these particles could be sorted out and framed into a thin film of transparent solid, one can readily conceive of the last subsiding particles—break-ethers pure and simple—yielding a body which appears sea-green by transmitted light and has a pinkish surface reflection.

In transparent coloured solids and in coloured solutions, however, there is no break of continuity. The break-ether is not distinguishable with the eye or with the most powerful microscope; prismatic light alone detects it. My observations go to prove that it is of the same order of magnitude as the ether wave itself. Thus we have seen that the beginnings of absorption in iodine violet solutions, or, in other words, the width of the break-ether of iodine, is 4000 tenth-metres.

Taking 5000 tenth-metres as a near approach to the mean length of a luminiferous ether wave, we may employ this as the unit in estimating the sizes of break-ethers. I have made the following determinations in the manner described for iodine:—

| | Size of break-ethers (unit 5000 tenth-metres). |
|---|---|
| Iodine, in violet solutions . | 0·80 |
| Permanganate of potash (3 central bands) . .. .. | 0·26 |
| Magenta .. .. .. .. | 0·09 |
| Iodine green . .. .. .. | 0·96 |
| Methyl violet, 3 B .. .. | 0·12 |

These substances exhibit isolated absorption-bands. The numbers vary with the intensity of the light used and with the dispersive power of the spectroscope. I have employed a paraffin oil lamp and a Browning's spectroscope with single dense glass prism.

The break-ether in yellow solutions or transparent solids will show its influence first in the violet or ultra-violet region of the spectrum; a number of them yielding absorption up to F give the following figures in the above units:—

| | |
|---|---|
| Iodine in yellow solutions .. .. | 2·4 |
| Bichromate of potash .. .. .. | 20·0 |

The "band-raising" power of different solvents in dissolving the same body, regarded from the break-ether standpoint, resolves itself into a difference of disintegrating or adhesive power of the solvents—one solvent producing smaller break-ethers than another. A comparison of violet iodine with violet iodine solutions (Chem. News, lxvii., p. 111) shows that the general absorption of the latter is raised towards the violet end of the spectrum, presumably because the break ethers of the dissolved iodine are of different size from those of the gaseous element.

The possible constitution of a break-ether has been shown in my note on the "Atomic Colour Cross" (Chem. News, lxv., p. 205). It is built up of atomic material of definite distribution in the table of the periodic or natural classification of the elements.

An increase in number of break-ethers increases the absorption of light (Chem. News, Oct. 5, 1877). The number may be increased either by (1) rise of temperature—the usual colour-changing phenomena; (2) increase of stratum, or depth, or strength of substance through which light is passing; or, (3), by changes similar to that of solid platinum or silver to the black finely-divided element obtained by chemical means.

Somewhat similar molecules, *i.e.*, molecules akin as in a natural series of compounds, constructed on the same plan, and varying in volume in definite order, must, one may presume, form similar aggregates of the break-ethers, varying but slightly, and that in gradations of dimensions such as to regulate the absorption of light in definite order, and therefore producing colour in definite order, and the relations of colour to constitution.

Since writing the first of these papers, the researches of Dewar have directed special attention to the properties of liquid oxygen. With its blue colour it falls naturally into its place in the sulphur series of elements (Chem. News, lxvii., p. 27) and also shows the relation of atomic volume if we take Wroblewsky's figure for the specific gravity, viz,, 1·24 at −200° C., the lowest temperature at which the sp. gr. appears to have been taken (*vide* Clarke's "Constants of Nature," Part 1, p. 8).

Halifax, March 20, 1893.

## THE DETECTION AND DETERMINATION OF ARSENIC.[*]

By JOH. THIELE.

(Concluded from p. 142).

In the first place the attempt was made to determine 0·12 grm. of arsenious acid in the apparatus, and by the method described with the use of 30 grms. pulverised zinc. The first absorbent vessel was charged with a solution of silver at 1 : 50, the second and the third with silver solutions at 1 : 10. On titrating the contents of these vessels with decinormal solution of iodine according to the method described, there was found only 95 per cent of the arsenic present, so that about 5 per cent remained in the generating-flask.

The result was quite different if a hydrochloric solution of stannous chloride was added to the contents of the flask through a tube funnel after the lapse of about an hour when the development of hydrogen is nearly at an end. In the moment when this solution fell into the clear liquid of the round flask there appeared a turbidity and then a dark precipitation. This turbidity and precipitate disappeared in a few minutes on adding a little platinum chloride to revive the liberation of hydrogen, and the liquid resumed its former appearance. Hereupon the flask was heated for about fifteen minutes, and a current of hydrogen free from arsenic was passed through the apparatus for the same length of time.

On determining the arsenic in the absorbent vessels, the entire quantity of arsenic was found, and the residue in the generating flask was found to be entirely free from arsenic.

The method conducted as just described allows, consequently, of a quantitative determination of the arsenic, and may be especially important in judicial investigations.

The author leaves it undecided whether on the addition of stannous chloride there takes place a combination of the metallic arsenic deposited with the precipitate of spongy tin forming tin arsenide, or whether the arsenic is present in the tin sponge in a finely divided metallic state.

The author has modified the apparatus above described as follows:—The round flask, containing 300 c.c., was connected with a Woulfe bottle holding 150 c.c., its gas inlet tube being provided with a Bunsen valve or a glass ball valve. This renders a reflux impossible, so that it is not necessary to observe the working of the apparatus continually. The Woulfe bottle was connected with three receivers holding 100 c.c. each, all containing solution of silver at 1 : 50, the Woulfe bottle containing as much as corresponded to the arsenic used for the experiment. The further precaution was taken that all the liquid was forced through the dropping funnel into the round flask by the pressure of hydrogen, whereby the ascent of gas bubbles into the dropping funnel is made impossible.

If the zinc used in the experiment is not perfectly free from arsenic, its proportion can be easily determined in the above apparatus and deducted from the results of the several experiments.

The author purposes ascertaining whether the method cannot be used for separating arsenic from antimony or for determining both elements when jointly present.

## THE ABSORPTION OF FREE NITROGEN BY PLANTS.

As soon as organic analysis was rendered capable of accuracy, a number of interesting questions could not fail to be raised. One of the most important—*the* weightiest, in fact—from a practical point of view, was the origin of the nitrogen found in plants. We weigh, *e.g.*, the total crop of wheat, or of beans, produced upon an acre of land. We take a fair average sample of the bulk, or, for the sake of greater accuracy, a number of such samples, and we determine with every precaution their percentage of combined nitrogen. From the result it is easy, of course, to calculate how much nitrogen has been present in the entire crop. Now comes the question: Whence have the plants obtained this nitrogen? We analyse the seed, and find a certain amount. We analyse in like manner the soil, including the manures which have been used. We determine the ammonia present in the air, in the rain, and in the ground-water. We add together all these quantities of combined nitrogen, and we find that the sum falls very considerably short of the combined nitrogen present in the crop.

This fact is fully recognised by Sir J. Lawes and Dr. Gilbert as a conclusion drawn from their prolonged and world-famed researches, and they admit that there must exist in nature a source of nitrate which science has not yet discovered, or, it might be added, has not yet appreciated.

As a confirmation of this truth, our attention is drawn to Alpine pastures. Their supply of nitrogenous matter is constantly drawn upon in the form of milk and cheese. Still the grass continues to grow and to nourish the cattle, although no nitrogenous manures—such as guano, nitre, ammonium sulphate, &c.—is ever applied. To say that the fertility of the soil is kept up by the dung and urine of the cows—as farmers of the old school still believe—is in reality to affirm the creation of matter. The excreta in question cannot possibly contain anything other or more than there was in the grass, *minus* the quantity sent away in the form of dairy produce. Hence the question is narrowed. Either the nitrogenous matter is obtained from the superabundant stock of free nitrogen existing in the atmosphere, or it must have its source in some unknown product, not hitherto identified, either in the soil, the air, or the water. But such a product, such an *x*, to play so wide and important a part, would have to exist, not in minute traces easily overlooked, but in relatively large quantities.

Hence we are driven back upon the free nitrogen of the atmosphere as the only conceivable resource: and here we enter the realms of the controversy. Men of science have, quite justifiably, demanded positive proof that the nitrogen of the air is thus absorbed and assimilated. The necessary experiments are, of course, delicate and tedious, and without special precautions it is worse than useless.

One o. the earliest experimenters in this direction was the celebrated Boussingault, who, as early as 1838, recognised the free nitrogen of the air as one of the three sources whence plants derived their supply of nitrogen. The other two sources admitted were the ammonia existing in the atmosphere—which is manifestly insufficient

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[*] From the *Zeit. Anal. Chemie.*

—and the dust suspended in the air—a supply which can scarcely come into serious consideration.

At this time M. Georges Ville took up the subject. In his experiments he showed that the nitrogen found in the plants exceeded, by several thousand times, the quantity which they could derive from atmospheric ammonia: and, as for dust, it was carefully excluded by special arrangements. Consequently, the nitrogen found in the crop in excess of that existing in the seeds could be due only to a fixation and absorption of the free gaseous nitrogen of the air.

It might have been expected that Boussingault would have welcomed M. Ville's verification and extension of his results. Nothing of the kind. Though the discovery of the assimilation of free nitrogen by plants had opened to him the doors of the Academy—though Dumas (*Comptes Rendus*, vi., p. 131) had accepted the proof that "clover absorbs the nitrogen of the air, and everything leads us to believe that this phenomena is general," yet, in 1852, Boussingault read before the Academy of Sciences a voluminous memoir in which he repeated *seventeen times* the words "the nitrogen of the air is not absorbed by plants." Yet all the time he proclaimed it an injustice when he was accused and convicted of this remarkable change of front. He asserted (*Comptes Rendus*, xxxviii., p. 719) that if he had proved anything in his former memoir it is that the gaseous nitrogen of the air was not fixed by vegetation in his last experiments.

Fortunately, in the scientific world at least, when a man formally eats his own words and denies what he has formerly asserted, and what has been accepted as his title of honour, he cannot carry the world with him. The late Abbé Moigno (*Cosmos*, iv., p. 561) thus clearly expounds the case:—

"1. The assimilation of the gaseous nitrogen of the air by plants, although M. Boussingault's demonstration was incomplete, was made known with such characters of evidence, surrounded with such a total of irrefragable confirmation, that it has been accepted with such a rational enthusiasm as to make it more than rash to seek at present to call it in doubt.

"2. The method of experimentation followed by Boussingault in his first experiments has been proclaimed so rational and so certain in its fundamental arrangements, so exact in its results, that, especially since M. Ville has so modestly completed it, so skilfully freed it from all the objections which might still be raised against it, there can no longer remain the shadow of a doubt as to the absolute reality of the fact which it places in evidence.

"3. Lastly, the new method followed by M. Boussingault is as bad as his first method was good if we suppose it completed. His recent experiments are as futile and as barren of conclusions to be drawn from them as his earlier experiments, when rightly interpreted, were convincing and fruitful."

We have yet to show in detail the misleading character of the later experiments undertaken by M. Boussingault.

## THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from vol. lxvi., p. 228.)

Some time ago we contributed an article on this subject,† and we now propose to complete our remarks on the question. In the former article we dealt with the subject in an introductory manner, and we now propose to discuss it in detail.

The complete practical analysis of iron and steel, as generally understood, comprises the determination of silicon, sulphur, phosphorus, combined and graphitic carbon, manganese, and, in some instances, of copper, titanium, chromium, tungsten, and oxide of iron. Before proceeding with the description of the methods employed for the determination of these several constituents, we wish to draw the operator's attention to two points which it is necessary to rigidly observe before results that can lay any claim to accuracy can be obtained, viz.:—(1) The reagents employed must be absolutely pure; and (2) strict cleanliness and the avoidance of dust, which, unless due precautions are taken, will accumulate during ignition, weighing, &c.

*Silicon.*—In the methods employed for the estimation of silicon in iron and steel, it must be oxidised into silica ($SiO_2$), and then collected and weighed. When the metal is treated with aqua regia or nitro-hydrochloric acid, the iron enters into solution as ferric chloride, while the silicon is oxidised into silica, which, upon evaporation of the solution and strong heating, is rendered insoluble.

As nitro-hydrochloric acid is constantly employed in the analysis of iron and steel, &c., a stock should be prepared. It is made by adding one part of pure nitric acid (sp. gr. 1·42) to three parts of pure hydrochloric acid.

For analysis, 4 grms. of the sample in the state of drillings should be carefully weighed out into a porcelain dish of 500 c.c capacity, covered with 50 c.c. of nitro-hydrochloric acid, the mouth of the dish being covered with a large watch glass to prevent loss by spurting, and the whole heated gently on a hot plate or sand bath. When the iron is of such a nature as will not allow of the sample being obtained as drilling, as, for instance, white iron, it should be reduced to a fine powder in a steel mortar. Some chemists advise that the drillings should be treated with boiling ether under a condenser, and subsequently dried at 100° C., the object being to extract the oil, grease, &c., with which it may have accidentally become contaminated. This is hardly necessary if ordinary care be exercised during its preparation. Silicon and graphite—especially the latter—appear to be unevenly distributed in grey pig iron. The drillings from such must therefore be very carefully mixed. Drillings not carefully mixed gave:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Silicon, per cent .. | 2·11 | 1·74 | 1·93 | 1·70 |
| Graphite, per cent .. | 3·00 | 3·50 | 3·37 | 3·80 |

Instances have been noted in which serious discrepancies have occurred between chemists, arising solely from the assumption that the sample of pig was of even composition throughout, and that drillings taken from any part would give like results. When it is judged that the whole of the iron is in solution, the watch glass must be removed, and washed by a fine stream of hot distilled water, in order to recover any of the solution which might have spurted on to the glass. The solution is then evaporated to complete dryness and heated strongly over a Bunsen burner until the residue is black—the heat of the sand-bath or hot plate not being sufficient. When the dish and contents are thoroughly cool, the residue is moistened with 60 c.c. of hydrochloric acid, and gently heated until all the iron is brought into solution, and the excess of acid expelled from the solution by carefully evaporating until a crust commences to form. At this point evaporation must be arrested, and the crust dissolved by the addition of a few drops of hydrochloric acid. To the solution thus obtained, five times its volume of hot distilled water are added, and the whole filtered through a good English filter-paper previously washed three times with a dilute solution of hydrochloric acid and several times with water. All filter-papers, previous to being used, should be subjected to this washing with acid and water. The paper retains the residue, consisting of silica ($SiO_2$) and, perhaps, graphite. The portions of the residue adhering to the sides of the dish are detached by

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* From *Industries*, January 27, 1893.

† See *Industries*, vol. vii., p. 211; also Chemical News, vol. lxvi., p. 228.

means of a "policeman," *i.e.*, a piece of caoutchouc tubing at the end of a glass rod, and rinsed into the filter. The filter-paper and contents are then washed, four times with a hot 10 per cent solution of hydrochloric acid, and afterwards repeatedly with water until a drop of the washings gives no red colour when brought in contact with a 5 per cent solution of sulphocyanide of potassium, several drops of which have been placed on a white porcelain slab. If a steel be under examination, the residue on the filter consists of silica ($SiO_2$); but if an iron, graphite or graphitic carbon is generally also present. The treatment of the filter and its contents depends therefore upon whether one or both of these constituents are present. If silica only be present, the filter-paper and contents are transferred to a porcelain or platinum crucible, ignited at a strong red heat, and, when cold, weighed. The weight, minus that of the filter-paper ash, gives the silica ($SiO_2$), which contains 46·66 per cent of silicon.

Several of the constituents of iron and steel are present in such minute quantities that an increase or decrease amounting to 1 or 2 m.grms. in the weights of the precipitates obtained in their determination make a considerable difference in the resulting percentages. It therefore becomes necessary to determine the amount of ash contained in the filter-paper employed, and to deduct it from the weights of the precipitates obtained.

In the presence of graphite, the filter-paper and contents are placed in a shallow porcelain dish, and the paper burnt off at the lowest heat possible (a high temperature would result in the graphite being burnt off also). When cold, the residue, consisting of silica and graphite, is weighed, replaced in the dish, and again ignited, this time at a bright heat. The graphite burns off, while the silica remains behind. When cold it is weighed and the amount deducted from the combined weights of the silica and graphite, the weight of the graphite thus being obtained.

Great difficulty is experienced in obtaining a pure white silica by this method, it being usually more or less coloured. This is especially the case with specimens containing considerable quantities of phosphorus, and it is then due in all probability to an insoluble phosphide of iron (Riley, *Chemical Journal*). Neither can the whiteness of the silica be taken as a guarantee of its purity, as, although free from iron, it may at the same time be contaminated to a considerable extent with titanium, if that metal is contained in the iron or steel. To obtain the silica in a pure state it is transferred to a platinum crucible, intimately mixed with six times its weight of acid potassium sulphate ($KHSO_4$), and fused. Upon cooling, the fused mass is broken up as completely as possible with the aid of a glass pestle. The crucible and contents are then placed in a porcelain dish and digested for a considerable time while constantly stirred with cold water. When the whole of the fused mass has dissolved, the crucible, after being well washed, is withdrawn, and the residual silica, now free from impurities, collected on a filter; or the silica may be volatilised by gently heating in a platinum crucible with hydrofluoric and sulphuric acids (both are essential), the residue weighed, and the silica estimated by difference.

The following method, while occupying considerably less time in its performance, furnishes results nearly as accurate as the one just described:—Four grms. of the sample contained in a beaker are treated with 60 c.c. of dilute sulphuric acid—1 part acid to 3 of water—the mouth of the beaker covered with a watch glass, and the whole placed on a hot plate or sand-bath. When the iron is dissolved, the watch glass, after being washed, is removed, and the solution evaporated until thick white fumes of sulphuric acid are given off. The evaporation is then arrested, and the beaker and contents allowed to cool. 100 c.c. of water are then added, and the whole heated to the boiling point, while constantly stirred, until the whole of the mass of anhydrous ferrous sulphate has been dissolved. The silica is then filtered off, together with some graphite probably, washed, &c. The purity of the silica thus obtained is determined by the method previously described.

(To be continued).

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## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 28th, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, March 12th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As a result of the excessive rainfall of the month, the condition of the metropolitan water supply during February, though not unsatisfactory for the period of the year, was found to compare somewhat unfavourably with that manifested in January, which was on the whole a dry month, despite a fall, as measured at Oxford, of over three-quarters of an inch during the last few days of the month, and so only affecting somewhat the early supply for February. The total rainfall for February, as measured at Oxford, was 2·64 inches, being 0·72 inch above the average, and constituting the month one of the wettest Februaries recorded for several years past.

But the more or less flooded state of the rivers during a large portion of the month, though having a prejudicial influence on the supply, more especially in respect to the degree of freedom from colour-tint, did not affect the proportion of organic matter present in the water to any such extent as to bring it into appreciable excess over the low winter average prevailing during the previous two months, as shown in the following Table. Moreover the mean ratio of organic nitrogen to organic carbon, or 21·5 to 100, was low, and indicative so far of the preponderating vegetable nature of the actually small proportion of organic matter present in the supply.

Of the total 168 samples of water examined during the month, two only were recorded as deficient in brightness, the remainder, despite the flooded state of the rivers, being found to be clear, bright, and well filtered.

| | Ratio of brown to blue tint. Means. | Oxygen required for oxidation. Means. | Organic carbon per 100,000. Means. | Organic carbon per 100,000. Maxima. |
|---|---|---|---|---|
| Previous two months .. | 23·6 : 20 | 0·068 | 0·198 | 0·286 |
| January .. .. | — : 20 | 0·052 | 0·159 | 0·248 |
| February .. | — : 20 | 0·069 | 0·201 | 0·269 |

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

# GRAVIMETRIC COMPOSITION OF WATER.[*]

By W. DITTMAR, LL.D., F.R.S., F.R.S.E., and J. B. HENDERSON.

(Continued from p. 141).

### *Second and Final Series of Syntheses.*

These we carried out after we had learned to prepare absolutely oxygen-free hydrogen: by passing the gas (after its deoxidation by red-hot metallic copper), over fused caustic potash, followed by phosphoric anhydride (instead of over vitriol) for its dehydration.[†] Let us state at once that the $P_2O_5$ tubes never gained weight appreciably, so that, as we now know, they might have been dispensed with.

While preparing for these final experiments we invented an easy method for obtaining a very perfect vacuum, by means of two ordinary pumps. An ordinary syringe, provided with a solid piston and a two way cock at the end of the barrel, was combined with a large bottle in which a fair ordinary vacuum was maintained by a second air-pump in such a manner that the waste air from the syringe instead of being sent into the atmosphere was discharged into the vacuum-bottle. By proceeding in this manner we easily succeeded in producing a vacuum of less than 1 m.m.; and yet we soon came to give up this refinement, because it turned out that the pump proper, when in good condition, exhausted to about 3 m.m. easily, and this sufficed for our purpose, because we took care to weigh both the metallic copper and the oxide of copper in a hydrogen-vacuum, besides measuring the pressures of our *vacua* by means of a specially constructed mercury gauze, shown at Fig. 8. (A rather large syphon-manometer, the vacuum limb of which was provided with a very good Greiner and Friedrich stopcock, while the open limb communicated with a mercury reservoir. As the tube was about a c.m. wide inside, it was easy to fill the instrument with mercury without introducing more than a trace of air, and the influence of this was reduced to a minimum by expanding the vacuum into the largest available space.) The construction of the reduction-tube is shown by Fig. 9, for the explanation of which it suffices to say that, during use, the joint at C was made tight by means of a close bandage of warm non-vulcanised indiarubber, secured by double wires both at the left and at the right of C, and that during the evacuations the end H was closed with an indiarubber cap as shown in the figure. J is a piece of red indiarubber tubing, K a rounded glass rod, L a glass cap fitting over the indiarubber. The indiarubber tube is closed at its lower end by means of copper wire, M. For the tightening of the indiarubber tube at J, two pieces of copper wire of exactly the same weight were provided, one served in the first exhaustion, the other in the second. The joints were found to hold very tight, only in the first rehearsal the rim of the reduction-tube cracked in consequence of the belt of the stopcock part being pressed against it by the atmosphere. This, however, in subsequent experiments, was easily avoided by placing a few small bits of card paper between the two glass surfaces. The tare for the reduction-tube was made out of a piece of combustion tubing of the same width as that for the working-tube. This tare tube was simply drawn out and closed at both ends, but its outer volume was so adjusted that it displaced exactly the same weight of water as the working tube did with its cap and stopcock on.

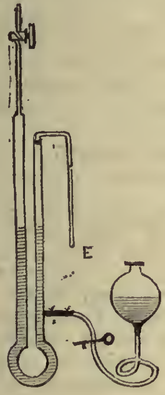

Fig. 8.

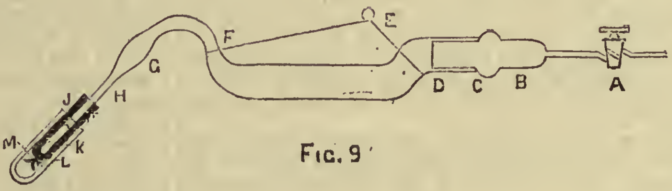

Fig. 9

We might have stated before that there is a stopper of asbestos at F, which was introduced for the first experiment and never taken out.

In a synthesis, the first step was to charge the reduction-tube with about 115 grms. of oxide of copper, and, after having attached the stopcock, to heat it in a magnesia bath in a current of dry air (about 4·5 litres). This, as a rule, was done on the day preceding the experiment. The tube was left overnight with the cock closed and the cap wired on, and on the following morning it was exhausted with the pump or combination of pumps. Hydrogen was then admitted into it, and the tube allowed to stand beside the balance while the other apparatus was being weighed. It was next exhausted as completely as possible (the vacuum meter being read this time) and weighed against its tare. After the attainment of constancy of weight, the tube was left suspended for at least ten minutes, to make sure that no air leaked in. From the beginning of the first to the end of the last weighing, the indiarubber joint at C was kept covered over with a piece of very thin silver foil to prevent change of weight as far as possible. During the progress of a reduction, the parts of the tube which were not meant to be heated were protected by suitable asbestos anhydride screens.

The water-receptacle was the same as the one which had been used in the first series, except that the U-tubes which followed it were charged, the first with fused caustic potash, the second with phosphoric anhydride. On account of the bulkiness, more than on account of the greater weight, of the reduction-tube, the small balance which we had used in the first series was not conveniently available this time. We substituted for it an excellent kilo balance from Oertling, which, like the smaller instrument used before, is provided with a Dittmar microscopic reading arrangement, and which, even when charged with several hundred grms. on each side, is constant in its indications to within 0·2 to 0·1 m.grm.

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[*] *Proceedings of the Philosophical Society of Glasgow.*

[†] The corresponding U-tubes were prepared in this way:—A quantity of asbestos was dehydrated by heating, then shaken in a bottle with an abundant supply of the anhydride, and quickly transferred to the U-tube after its bend had been about half filled with the reagent.

On account of the introduction of the vacuum method for the determination of the oxygen, the execution of the experiments was not quite so easy as in the first series, and it took us some time before we became quite familiar with all the manipulations involved. But there would be little use in here giving exact instructions in regard to minor details. Whoever cares to repeat our experiments must go through his own apprenticeship.

In now proceeding to report on the individual experiments, we shall, for brevity's sake, use the following symbols:—

$S$ for the loss of weight suffered by the reduction-tube.

$m'$ and $m''$ for the tension of the hydrogen, in which the CuO and Cu were weighed, respectively.

$S_0$ for the corrected weight of the oxygen. As a rule $S_0 = S$.

$w_0$ for the uncorrected weight of the water obtained in the liquid form.

$w'$ and $w''$ for the uncorrected weights of the steam condensed in the caustic potash tube following the water-receptacle, and in the $P_2O_5$ tube following the KHO tube respectively.

$t''$ for the temperature, and $P''$ for the pressure, of the atmosphere at the second weighings.

"Air" for the weight of air displaced by the $w_0$ grm. of liquid water.

$W$ for the total weight of water uncorrected; $W_0$ for the same corrected.

$h_0$ for the weight of hydrogen $= W_0 - S_0$.

$H$ for $8 \times (h_0 : S_0)$; that is to say, the atomic weight of hydrogen referred to $O = 16$.

*Experiment* (1). $S = 17{\cdot}0530$; $m' = 7$ m.m.; $m'' = 5$ m.m.; hence $S_0 = S$. $w_0 = 19{\cdot}0367$. $w' = 0{\cdot}1457$. $w'' =$ nil. Hence $W = 19{\cdot}1824$; $t'' = 11{\cdot}75°$; $P'' = 748{\cdot}9$ m.m. Hence, air displaced by the $w_0$ grms. of liquid water $= 23{\cdot}3$ m.grm.; and $W_0 = 19{\cdot}2057$, and $h_0 : S_0 = 0{\cdot}126\,236$, and $H = 1{\cdot}009\,89$.

There was a little difficulty in getting the last drop of water out of the drawn-out end of the reduction-tube into the water-flask; otherwise the experiment proceeded quite normally.

*Experiment* (2). In this experiment everything proceeded quite normally except that, at the end, when the reduction-tube and water-flasks were detached from each other, a minute drop of water was seen adhering to the end of the neck of the former. Rather than simply neglect this water, or lose the experiment, we produced as good an imitation as we could of the droplet at the end of a tared glass tube, similar to the neck referred to, and weighed it. It amounted to 4·3 m.grm. Allowing this as a correction for the water-weight directly found we had $S = 17{\cdot}3342$; $m' = 3{\cdot}5$ m.m.; $m'' = 5{\cdot}0$ m.m. $S_0 = S$. $w_0 = 19{\cdot}4403$; $w' = 0{\cdot}0568$; $w'' = 0$. Hence $W = 19{\cdot}4971$. $t'' = 11{\cdot}5°$; $P'' = 756{\cdot}6$ m.m. Hence air displaced $= 24{\cdot}0$ m.grm., and $W_0 = 19{\cdot}5211$, whence $h_0 : S_0 = 0{\cdot}126\,161$, and $H = 1{\cdot}00929$.

If we neglect the drop of water lost we have $h_0 : S_0 = 0{\cdot}125912$, and $H = 100731$.

*Experiment* (3). $S = 17{\cdot}2882$; $m' = 6{\cdot}0$; $m'' = 6{\cdot}0$ m.m. Hence $S_0 = S$. $w_0 = 19{\cdot}3892$; $w' = 0{\cdot}0544$; $w'' = 0{\cdot}0001$. $W = 19{\cdot}4436$. $t'' = 13°$; $P'' = 748{\cdot}9$. Hence air $= 23{\cdot}6$, and $W_0 = 19{\cdot}4672$, whence $h_0 : S_0 = 0{\cdot}126040$, and $H = 1{\cdot}00832$.

*Experiment* (4) was lost through the pressure of the atmosphere driving the stopcock part of the reduction-tube against the receptacle of the oxide and causing it to crack.

*Experiment* (5). In this experiment the air-pump failed to work properly, so that the pressure in the reduction tube could not be reduced to less than 27 m.m. Otherwise everything went on all right.

$S = 20{\cdot}3540$; $m' = m'' = 27{\cdot}0$ m.m. Hence $S_0 = S$. $w_0 = 22{\cdot}8360$; $w' = 0{\cdot}0630$; $w'' = 0{\cdot}0002$. Hence $W = 22{\cdot}8992$. $t'' = 13°$; $P'' = 754{\cdot}0$. Hence air $= 28{\cdot}0$, whence $W_0 = 22{\cdot}9272$, and $h_0 : S_0 = 0{\cdot}126422$, and $H = 1{\cdot}01138$.

*Experiment* (6). In this experiment the air-pump again failed to work satisfactorily, and, as a consequence, the two readings of the manometer were inconveniently high, and, what is worse, different from one another. The experiment otherwise proceeded all right.

$S = 20{\cdot}4418$; $m' = 15$; $m'' = 40$ m.m.; corresponding correction $= +0{\cdot}26$ m.grm. Hence $S_0 = 20{\cdot}4421$. $w_0 = 22{\cdot}9232$; $w' = 0{\cdot}0565$; $w'' = 0{\cdot}0002$. Hence $W = 22{\cdot}9799$. $t'' = 14{\cdot}8°$; $P'' = 758{\cdot}6$. Hence air $= 28{\cdot}1$; $W_0 = 23{\cdot}0080$; $h_0 : S_0 = 0{\cdot}125521$; and $H = 1{\cdot}00417$.

*Experiment* (7). $S = 20{\cdot}8639$; $m' = m' = 18$ m.m. Hence $S_0 = S$. $w_0 = 23{\cdot}4059$; $w' = 0{\cdot}0608$; $w'' = 0$; $W = 23{\cdot}4667$. $t'' = 15{\cdot}3°$; $P'' = 751{\cdot}7$. Hence air $= 28{\cdot}4$; and $W_0 = 23{\cdot}4951$; $h_0 : S_0 = 0{\cdot}126112$; and $H = 1{\cdot}00890$.

*Experiment* (8). In this experiment the reduction-tube cracked just before its second exhaustion, hence the metallic copper had to be weighed in hydrogen at the pressure of the atmosphere. We had:—$S = 20{\cdot}1952$; $m' = 18$ m.m.; $m'' = 752{\cdot}0$; calculated correction $= +7{\cdot}4$ m.grm. Hence $S_0 = 20{\cdot}9226$. $w_0 = 23{\cdot}4745$; $w' = 0{\cdot}0578$; $w'' = 0{\cdot}0005$. Hence $W = 23{\cdot}5328$. $t'' = 15{\cdot}5°$; $P'' = 752{\cdot}0$. Hence air $= 28{\cdot}4$, whence $W_0 = 23{\cdot}5612$; $h_0 : S_0 = 0{\cdot}126112$; and $H = 1{\cdot}00890$.

*Experiment* (9). $S = 21{\cdot}0957$; $m' = m'' = 3$ m.m. Hence $S_0 = S$; $w_0 = 23{\cdot}6543$; $w' = 0{\cdot}0714$; $w'' = 0$, whence $W = 23{\cdot}7257$. $t'' = 15{\cdot}5°$; $P'' = 747{\cdot}4$. Hence air $= 28{\cdot}5$; $W_0 = 23{\cdot}7542$; $h_0 : S_0 = 0{\cdot}126021$; and $H = 1{\cdot}00817$.

*Experiment* (10). $S = 21{\cdot}8994$; $m' = m'' = 2$ m.m. Hence $S_0 = S$; $w_0 = 24{\cdot}5870$; $w' = 0{\cdot}0400$; $w'' = 0$. Hence $W = 24{\cdot}6270$. $t'' = 15°$; $P'' = 752{\cdot}0$, whence air $= 29{\cdot}8$; $W_0 = 24{\cdot}6568$; $h_0 : S_0 = 0{\cdot}125912$; and $H = 1{\cdot}00730$.

*Experiment* (11). $S = 21{\cdot}8593$; $m' = 1{\cdot}5$; $m'' = 1{\cdot}0$ m.m. Hence $S_0 = S$. $w_0 = 24{\cdot}5407$; $w' = 0{\cdot}0474$; $w'' = 0$; $W = 24{\cdot}5881$. $t'' = 15{\cdot}0°$; $P'' = 751{\cdot}5$. Hence air $= 29{\cdot}8$; $W_0 = 24{\cdot}6179$; $h_0 : S_0 = 0{\cdot}126198$; and $H = 1{\cdot}00959$.

*Experiment* (12). $S = 21{\cdot}8499$; $m' = 2{\cdot}5$; $m'' = 2{\cdot}0$ m.m. Hence $S_0 = S$. $w_0 = 24{\cdot}5067$; $w' = 0{\cdot}0654$; $w'' = -0{\cdot}0001$; $W = 24{\cdot}5721$. $t'' = 15{\cdot}75°$; $P'' = 761{\cdot}4$. Hence air $= 30{\cdot}0$; $W_0 = 24{\cdot}6021$; $h_0 : S_0 = 0{\cdot}125959$; and $H = 1{\cdot}00768$.

*Experiment* (13). $S = 21{\cdot}5788$; $m' = 1{\cdot}7$; $m'' = 2{\cdot}0$ m.m. Hence $S_0 = S$. $w_0 = 24{\cdot}2118$; $w' = 0{\cdot}0631$; $w'' = 0$; $W = 24{\cdot}2749$. $t'' = 14{\cdot}9°$; $P'' = 761{\cdot}1$. Hence air $= 29{\cdot}8$; $W_0 = 24{\cdot}3047$; $h_0 : S_0 = 0{\cdot}126323$; and $H = 1{\cdot}01059$.

*Experiment* (14). $S = 20{\cdot}9709$; $m' = 3{\cdot}5$; $m'' = 3{\cdot}7$ m.m. Hence $S_0 = S$. $w_0 = 23{\cdot}5422$; $w' = 0{\cdot}0461$; $w'' = -0{\cdot}0001$; $W = 23{\cdot}5883$. $t'' = 15{\cdot}2°$; $P'' = 760{\cdot}6$. Hence air $= 28{\cdot}9$; $W_0 = 23{\cdot}6172$; $h_0 : S_0 = 0{\cdot}126189$; and $H = 1{\cdot}00951$.

(To be continued).

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**Oxidising and Decolourising Action of Charcoal.**—Çazeneuve (*Pharm. Central Halle*).—As far back as 1874 A. W. von Hofmann observed that charcoal—especially animal charcoal—can exert a strong oxidising action. An alcoholic solution of leukaniline quickly yields rosaniline if boiled with animal charcoal. Cazeneuve made similar observations on boiling aqueous solutions of α-naphthylamine or of paraphenylendiamine with animal charcoal; the first mentioned becomes a purple red and the second a brown. The charcoal retains the colour firmly, but yields it up again to boiling alcohol. The idea that the oxidising action of carbon was concerned in the decolourising action was at once suggested. On experiments made for this purpose it was found that charcoal which had been previously ignited and cooled in a current of dry nitrogen or in carbon dioxide had less decolourising power than such as has been cooled in the air. Cazeneuve is of opinion that the residual oxygen in the charcoal burns the colouring-matter.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, March 2nd, 1893.*

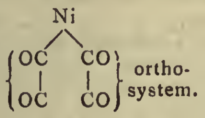
Dr. J. H. Gladstone, F.R.S., Vice-President, in the Chair.

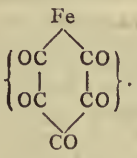
(Concluded from p. 145).

*124. "*Note on Optical Properties as Indicative of Structure.*" By Henry E. Armstrong.

In his "Notes on some Recent Determinations of Molecular Refraction and Dispersion," recently communicated to the Physical Society (*Phil. Mag.*, 1893, 203), Dr. Gladstone directs attention to a number of curiously suggestive observations of special interest in connection with the all-fascinating enquiry into the correlations of properties and structure. The metallic carbonyls to which he refers, in respect of physical properties as in many other respects, are compounds of extraordinary interest. The conclusion which both Mond and Gladstone favour that they are cycloids is undoubtedly that most in harmony with their general behaviour, affording as it does an explanation of the complete masking of the metal, comparable, for example, with that which sulphur suffers in thiophen.

The excessive refractive and dispersive power which the metallic carbonyls exhibit is probably, as Gladstone suggests, to be sought in the peculiar arrangement of the carbonyls; one object of this note is to call attention to the evidence which the optical data apparently afford of their *co operative action.* The ketonic compounds hitherto studied from which the value CO = 8·4 has been derived have been compounds containing single or isolated carbonyls, whereas—if represented as cycloids—the metallic carbonyls contain two "ortho-systems," thus—





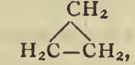
In this sense they are in fact diorthoquinonoid, and are comparable with coloured substances, but they are not truly quinonoid, the cycloid being saturated, and hence should not be coloured. (The nickel compound is colourless, but the iron compound is described as yellow; the instability of the latter, however, is such that this colour may be due to impurity). There are only two orthoquinonoid systems, although there are five carbonyls in iron pentacarbonyl, so that one of the carbonyls should have the ordinary value and only four the value they apparently exhibit in nickel tetracarbonyl (11·9): consequently the molecular refraction should be—

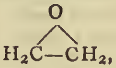
4CO (orthoquinonoid) = 4 . 11·9 = 47·6
CO (ketonic) = 8·4
Fe″ = 11·6
67·6

a value not far removed from that found, viz., 67·4.

If this argument be a sound one, it is to be anticipated that quinonoid compounds generally will be found to possess specially high refractive powers; and there is some evidence that this is the case: thus among the compounds examined by Gladstone (*Chem. Soc. Journ.*, 1870, 101—147; *Trans.*, 1884, 241) anthracene—a hydrocarbon which, as more than once pointed out, is probably quinonoid in structure—is credited with a very high value, considerably above that calculated even if the value 6·1 be assigned to carbon. Gladstone has also stated that β-nitraniline has an abnormally high refractive power. I learn from Professor Mills that the compounds referred to as α- and β-nitraniline which he gave to Gladstone were the meta- and para-derivatives; apparently, therefore, this result is in accord with the view previously advocated (*Proc. Chem. Soc.*, 1892, 101), that paranitraniline and similar *coloured* nitro-compounds are in reality quinonoid. Dr. Gladstone states, however, that both substances were examined in weak solutions, and, therefore, less than the usual confidence can be felt in the accuracy of the data.

Liveing and Dewar's determination of the molecular refraction of nitrous oxide in the liquid state is also referred to by Gladstone, who points out that the value observed (11·418) favours the view that the nitrogen in nitrous oxide has the low value which this element exhibits in nitriles, viz., 4·1. The determination of the structure of nitrous oxide is of special importance, as it is one of a group of compounds, including trimethylene, ethylene oxide, and diazoimide, all of which it is the fashion at the moment to formulate as cycloids:—



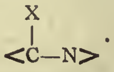


But apparently there is no valid evidence to justify the practice, and it is in no way necessary to adopt such a course. Unfortunately we are without knowledge of the optical properties of trimethylene, but we have J. Thomsen's remarkable observation that its heat of combustion exceeds that of the isomeric propylene by 6690 units. I have on several occasions discussed the properties of this hydrocarbon, and have pointed out how its unique behaviour with bromine and bromhydric acid may be explained by electrolytic considerations (*cf.* Morley and Muir's "Watts' Dictionary of Chemistry,' iii., Art. "Isomerism.") Granting the accuracy of Thomsen's figures, there appears to be no way of avoiding the conclusion that it is an open chain hydrocarbon, and, therefore, that free affinities may exist at the end of a chain; its dissimilar behaviour towards bromine and bromhydric acid precludes the application of von Baeyer's explanation of the instability of a ring of three atoms, as such a ring should prove unstable to bromine as well as to bromhydric acid, the former being in all other cases the more active agent in attacking hydrocarbons.

Ethylene oxide, in like manner, has an abnormally low heat of formation; in fact, on this account, J. Thomsen has gone so far as to represent it by the formula $CH_2\cdot O\cdot CH_2$, an expression offending against all recognised canons. If, however, trimethylene be written $CH_2\cdot CH_2\cdot CH_2$, ethylene oxide may be written $CH_2\cdot CH_2\cdot O$. Perkin's results, referred to in a previous note (*ante*), show that it is abnormal in its optical behaviour; they are most significant as affording evidence—assuming an open chain formula—that the optical effect of free affinities is below the normal, and it may be anticipated that trimethylene will afford low values. It is worth noting that carbonic oxide, in which we believe that certain of the affinities of the carbon atom, if not free, are "self engaged," has a molecular refraction (7·5) considerably below the value of CO in ketonic compounds: it would seem that the ordinarily accepted refraction equivalents are not to be regarded as measures of the effect of the "affinities" proper, but of the affinities *engaged between atoms.*

Passing now to the nitriles and nitrous oxide, we have the most indefinite ideas as to the former: they are conventionally represented as compounds of triad nitrogen, but this practice is but the outcome of formal obedience to certain artificial and dogmatic rules of valency, and has no real justification. As we must admit the existence of latent affinities in carbonic oxide—which may be written <CO—we may also admit the possibility of their

existence in nitrogen, and may represent the nitriles as compounds of the form—



$$\begin{array}{c} X \\ | \\ <C-N> \end{array}.$$

Nitrous oxide, on this assumption, would be—

$$<N-O-N>.$$

Diazoimide might, in like manner, be regarded as—

$$<N-NH-N>,$$

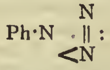
a formula which is implied in Mendeleeff's assumption that it is dinitrile. No diazoimide derivatives have hitherto been examined: Dr. Perkin had the kindness to determine the refractive power of the phenyl derivative, of which a quantity was placed at my disposal by Prof. Tilden: the results are as follows:—

*d* 10°/10° 1·0980; *d* 15°/15° 1·09318; *d* 25°/25° 1·08527.

| | *t.* | *n.* | $\frac{n-1}{d}$. | $\frac{n-1}{d}$P. |
|---|---|---|---|---|
| A .. .. | 11·7 | 1·54719 | 0·49943 | 60·431 |
| C .. .. | 11·7 | 1·55407 | 0·50571 | 61·191 |
| D .. .. | 11·7 | 1·56063 | 0·51170 | 61 916 |
| F .. .. | 11·7 | 1·57793 | 0·52749 | 63·826 |

Deducting from the value of aniline, 52·09, the value of two hydrogen atoms, 2·6, and adding twice the highest value of nitrogen, 2 . 5·1, the theoretical value is A = 59·89, which is lower by 0·54 than that found; so that diazophenimide has proportionally a somewhat higher molecular refraction than even aniline.

These results do not indicate that diazophenimide is a dinitrile; neither is it possible to deduce from them any special argument in favour of the formula—



$$\mathrm{Ph{\cdot}N} \begin{array}{c} N \\ \| \\ <N \end{array}:$$

the problem, in fact, remains unsolved.

Consideration of the facts makes it appear probable that a solution of the difficulty *may* be found, and not only so, but that it may be possible ere long to carry on the enquiry into the inter-relationship of structure and physical properties on more fruitful lines than has of late been possible.

In the case of paraffinoid compounds generally, both carbon and hydrogen seem to have a fixed optical value, and it may be supposed also that this is true of hydrogen in all cases; seemingly also, *ethenoid carbon*—carbon as it is in ethylene, whatever may be the mode in which the atoms are united—has a constant value. The variations which are noticed in paraffinoid and ethenoid derivatives must on these assumptions be ascribed to variations in the radicles displacing hydrogen; and it should be easy therefore, by studying a considerable number of properly chosen compounds, to determine which radicles are, and which are not, subject to variation and the circumstances which condition variation.

In the case of benzenoid compounds, there is no evidence of constancy. Even in the case of the hydrocarbons the value of the $C_6$ group rises from C = 6 (very nearly) in benzene to C = 6·15 in mesitylene, the only apparent alteration made consisting in introducing methyl in place of hydrogen. As all the evidence derived from the study of paraffinoids seemingly shows that $CH_3$ has an invariable value, it is only logical to suppose that the variation arises in the cycloid; in other words, that whereas the ethenoid $C_2$ system apparently has an invariable optical effect, the benzenoid $C_6$ system has a variable optical effect. There is nothing surprising in this conclusion—it is in absolute accordance with the experience derived from the study of the chemical behaviour of the benzenoid compounds. The variation, in many cases, is very considerable: that of aniline, for example, which has a molecular refractive power A = 52·09. Assuming $NH_2$ to be 5·1 + 2 . 1·3 = 7·7, and deducting the value of 5H = 6·5, the value of $C_6$ in aniline is 52·09 − 7·7 − 6·5 = 37·89, and C = 6·31. There is no reason why the value should not be still higher in diazophenimide: to determine the value of the $N_3$, either $N_3H$ or one of its paraffinyl derivatives should be examined. The chemical properties of diazophenimide are such—its nitro-derivatives are hydrolysed with such facility—as entirely to justify the assumption that the $N_3$ has a very special influence on the properties of the cycloid.

The strongest confirmation of the view here put forward is afforded by diphenyl, in which each carbon apparently has the value 6·39: the two radicles of which this hydrocarbon is composed being alike, and being both benzene residues and directly conjoined—putting the hydrogen aside—there can be no question that the variation is due to the variation in the optical effect of the $C_6$ group.

If it can thus be shown either that the ethenoid group has an invariable effect whatever number of such groups may be present in the compound, or that its effect is invariable except in certain cases in which a co-operative effect is traceable, and the benzenoid group be proved to have a variable optical effect, the most absolute demonstration will have been secured of the existence in benzenoid compounds of a peculiar structure such as is foreshadowed in the centric formula first proposed by me in February, 1887.

The following may be referred to as illustrative of the problems requiring consideration. Among haloid compounds, methylene iodide is altogether peculiar, its refraction equivalent (58·22) being much above the calculated value (52·1); this may be a case of co-operative action. The high dispersive power of carbon bisulphide is perhaps to be accounted for in some such manner. In iodoform, an eminently remarkable substance on account of its *colour* and other exceptional properties, the third iodine atom appears to exert an influence comparable with that of an ethenoid group in quinone, and to determine the appearance of colour. In this case the effect is seemingly produced within the sphere of affinity around the carbon atom, much as in the case of quinonoid compounds it is produced within the cycloid sphere of affinity. Bromopicrin, if the value found by Gladstone be correct, appears to be an example involving a negative influence, a cause which perhaps also prevails in the case of acetylenic compounds, the abnormally low refractive power of which is highly remarkable. The aldehyds offer many peculiarities. It is to be remembered that Thomsen has represented aldehyd as $CH_3{\cdot}C(OH)$; the oxygen in such a compound would have a lower value than in ketones, but the one atom of carbon, being in the carbonic oxide or dyad state, would probably have a lower value than 5; so that, by assigning the full value to both carbon atoms and the ketonic value to oxygen, the equivalent would be over-estimated. But no indication that such is the case is actually afforded by aldehyd.

The refraction equivalent of benzaldehyd is about two, and that of salicylic aldehyd about three, units above the calculated value; this may be due to an increase in the cycloid value, but it is conceivable that the cycloid and the ketonic groups in some way co-operate; and it is even possible to represent salicylic aldehyd as a quinonoid compound. It is noteworthy that both these aldehyds are very active substances, and prone to yield condensation products. Cinnamic aldehyd is one of the most refractive and dispersive of known substances, and its refraction equivalent (75·3) is much above the calculated value, 65·4. It may be represented as—

$$C_6H_5{\cdot}CH{\subset\!\supset}CH{\cdot}C{\subset\!\supset}OH,$$

or even as $C_6H_5{\cdot}CH{\subset\!\supset}C{\subset\!\supset}CH{\cdot}OH$, and it would seem probable that the high refractive power is conditioned by a co-operative influence of the contiguous cycloid and ethenoid groups. From this point of view, it is important to examine allene, $CH_2{\subset\!\supset}C{\subset\!\supset}CH_2$. Stilbene,—

$$C_6H_5{\cdot}CH{\subset\!\supset}CH{\cdot}C_6H_5,$$

is another equally striking instance, its refraction equivalent (113·39) being also very much higher than the calculated value (101).

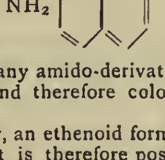
The arguments here made use of in correlating optical properties and structure are undoubtedly applicable to the discussion of other physical properties, and as some of these are apparently the measure of intra- and others of extra-molecular effects, it is all important that a careful comparison should be made with the object of elucidating reciprocal relationships.

In conclusion, attention may be directed to the *anomalous colour dispersion* displayed by rosaniline and other colouring-matters. In these compounds the two C⊂⊃R'' groups are of totally distinct types, and apparently the effect has not been noticed in the case of compounds in which the quinonoid groups are alike or similar. Biot has shown that the phenomena of anomalous *rotatory* dispersion exhibited by tartaric acid solutions are simulated by a mixture of two optically active mutually indifferent substances having different rotatory dispersive powers; it seems not improbable that the two dissimilar quinonoid groups which condition colour in rosaniline and substances which behave like it condition anomalous colour dispersion in consequence of their dissimilarity.

125. "*The Origin of Colour.* (IX.) *Note on the Appearance of Colour in Quinoline Derivatives and of Fluorescence in Quinine.*" By Henry E. Armstrong.

The arguments put forward in the previous note have far-reaching consequences. The increase in refractive power observed on comparing the homologues of benzene with benzene might be ascribed to a passage from the centric to the ethenoid form—assuming the former to have a slightly lower optical value than the latter; and such a view would be in accordance with the observed change in chemical behaviour, but it would not account for the change in the case of aniline and other compounds, as the optical value of carbon in these rises above that which is seemingly characteristic of the ethenoid form.

That the change takes place in some cases there can be little doubt, especially when von Baeyer's researches are taken into account. The object of the present note is to point out that its occurrence would account for the appearance of fluorescence and colour in quinoline derivatives which has been discussed in a previous note (*Proc. Chem. Soc.*, 1892, 143). Assuming quinoline to be a centric cycloid, and that the introduction of $NH_2$ has a very marked effect, as in the case of aniline, it is possible that the compound may thereby be caused to acquire an ethenoid structure; but such an ethenoid compound would be quinonoid, as may be seen on reference to the formula—



;

in other words, any amido-derivative of quinoline might be quinonoid, and therefore coloured, probably either orange or red.

In like manner, an ethenoid form of naphthalene would be quinonoid; it is therefore possible that the fluorescence exhibited by many naphthol and naphthylamine derivatives is characteristic of the pure substances, and does not always originate in impurities.

If the argument here used be justified, the non-appearance of colour and fluorescence in naphthalene derivatives will afford evidence of a centric structure similar in character to that which the peculiar optical behaviour of benzenoid compounds affords of a special structure different from the ethenoid form in benzene.

### Discussion.

The Chairman (Dr. Gladstone) said that he would like to consider the suggestive remarks of Prof. Armstrong on molecular refraction more carefully before committing himself to a definite opinion; the idea of a "co-operative influence," such as had been put forward, was, he thought, worthy of all attention. It had long struck him as an unexplained phenomenon, that while in the aromatic substances in general 6·1 is indicated as the atomic refraction of each of the double linked carbons, the value was very appreciably lower in benzene itself and in toluene; and that when the compound becomes very complex, the value becomes larger than 6·1. Thus aniline is certainly more refractive than would be anticipated from the usual run of benzene compounds and compound ammonias. Carbon in such compounds as naphthalene or phenanthrene has a much higher refractive power, to which he had, some years ago, provisionally assigned the value of 8·8. It had been remarked that the ethylene bonds in open chain compounds ought to retard light differently from the double bonds in the aromatic series. This was not to be easily recognised in the refraction of A, but it was, undoubtedly, the case in the dispersion. Such considerations must have much weight in the discussion of the structure of carbon compounds exhibiting special properties.

Dr. Perkin said, in reference to Dr. Armstrong's remarks on the very high values obtained for the refractive power of the carbonyl compounds of nickel and iron, it must be remembered that these compounds were examined in the pure condition, whereas all other determinations of the refractive power of nickel and iron were made with dissolved salts and do not necessarily give true values for these metals. In the case of zinc compounds he had found that the value of this metal in zinc ethyl was 15·9, whereas solutions of zinc salts gave only 9·8. Therefore it was not safe to infer that in the carbonyl compounds nickel and iron had the values they apparently possessed in salts. Through the kindness of Mr. Mond, he had had the opportunity of measuring the magnetic rotation of the nickel and iron carbonyl compounds, and had found that they gave very high rotations; but at present no other compounds of these metals had been examined.

As to the values given for the refraction of carbon and hydrogen being perfectly constant, even in saturated compounds this appears to be doubtful. Taking the case of ethylene oxide, they must be somewhat lower than usually given, and, in some of the amines, they appear to be higher; this is seen on comparing primary and tertiary amines, the refraction, but more especially the dispersion, increasing as we pass from the former to the latter. In the aromatic series this is very evident. Aniline itself has an abnormally high value, but, as methyl is introduced into this compound, the refraction increases with each methyl introduced much more than the change of composition requires, the increase for the first methyl being 8·36, and the change of dispersion no less than 1·37, and that for the second methyl 8·51, and of dispersion 1·22; whereas the calculated difference in each case is 7·6 only, and for the dispersion 0·34. Corresponding results are observed in reference to the magnetic rotation of all these compounds, though in a much more striking manner.

Dr. Armstrong had also made reference to the refractive power of two nitranilines; that these should be high is only consistent with their being derivatives of aniline. As to whether the difference of position of the $NO_2$ group would influence the refractive power of these substances in any marked degree, the data we have would be against such an assumption. Dr. Gladstone had measured several series of ortho-, meta-, and para-compounds at his request, and had found them to give nearly identical results.

Mr. Mond drew attention to the very different values deducible for nickel, the atomic refraction calculated from Kundt's observations with the metal being 6·12, while that calculated from the oxide is 9·82 (*cf.* Mond and Nasini, *Zeit. Phys. Chem.*, viii., 150).

### *Ethereal Salts of Glyceric Acid.*

*Inactive.*

| Ethereal salt. | Density, 15°/15°. | Difference. | Boiling-point. |
|---|---|---|---|
| Methyl .. .. .. .. | 1·2814 | 0·0905 | 119—120° (14 m.m.) |
| Ethyl .. .. .. .. | 1·1909 | | 120—121° (14 m.m.) |
| Propyl (normal) .. .. | 1·1453 | 0·0456 | 126—127° (14 m.m.) |
| Isobutyl .. .. .. .. | 1·1024 | — | 128—130° (13 m.m.) |

*Active.*

| Ethereal salt. | Density, 15°/15°. | Difference. | Observed rotation in 198·4 m.m. tube, α. | Specific rotation, [α]D. | Molecular rotation. $\frac{M. [\alpha]_D}{100}$ | Deduced specific rotation of glyceric acid ($C_3H_6O_4$), [α]D. | Boiling-point. |
|---|---|---|---|---|---|---|---|
| Methyl .. .. | 1·2798 | 0·0877 | −12·2° | − 4·80° | − 5·76° | − 5·43° | 120° (13 m.m.) |
| Ethyl .. .. | 1·1921 | | −21·7 | − 9·18 | −12·30 | −11·60 | — |
| Propyl (normal) | 1·1448 | 0·0473 | −29·4 | −12·94 | −19·15 | −18·07 | — |
| Isopropyl .. | 1·1303 | 0·0293 | −26·5 | −11·82 | −17·49 | −16·50 | 114—116° (13 m.m.) |
| Butyl (normal) . | 1·1155 | 0·0252 | −24·4 | −11·02 | −17·85 | −16·84 | 131—139° (14 m.m.) |
| Isobutyl .. .. | 1·1051 | | −31·2 | −14·23 | −23·05 | −21·75 | — |
| Butyl (secondary) | 1·1052 | | −23·2 | −10·58 | −17·14 | −16·17 | 123—126° (13·5 m.m.) |

*126. "*The Ethereal Salts of Glyceric Acid, Active and Inactive.*" By Percy Frankland, Ph.D., B.Sc., F.R.S , and John MacGregor, M.A.

The accompanying table contains the names of the glycerates, inactive and lævorotatory, which the authors have prepared, together with their densities, observed specific and molecular rotations, as well as the specific rotation of glyceric acid as deduced from the rotations of the several salts.

The method of preparation adopted for the methylic, ethylic, normal propylic, and normal butylic glycerates consisted in heating glyceric acid (either inactive or active) with an excess of the particular alcohol in a sealed tube at about 180° C., and then fractioning the resulting products by distillation under greatly reduced pressure. In the case of the secondary alcohols, this method yielded an unsatisfactory result, and consequently the isopropylic and secondary butylic salts were prepared by saturating a mixture of glyceric acid and the alcohol in question with hydrogen chloride gas, and then fractioning under reduced pressure. This method was also adopted in the case of isobutylic glycerate, although this compound could also, doubtless, have been satisfactorily prepared by the sealed tube method. It was found that the facility of etherification was much greater in the case of the primary than in that of the secondary alcohols, whilst in the case of the tertiary butyl alcohol (the only tertiary alcohol experimented with) it was not found possible to obtain an ethereal salt.

In preparing the isopropylic and secondary butylic salts, a considerable quantity of a white substance was formed which was found to be an anhydride of glyceric acid, whilst in the attempt to prepare the tertiary butylic salts, this anhydride appeared to be the sole product.

The active ethylic glycerate was prepared by both the sealed tube and hydrogen chloride methods, and the resulting products were found to have the same rotatory power, thus showing that the activity is in no way impaired by the high temperature (180° C.) employed in the sealed tube method.

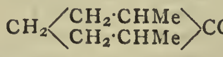
Attention is directed to the relationship between the molecular rotations of the several glyceric ethereal salts experimented with. This rotation increases almost quite regularly from methylic to ethylic, to normal propylic glycerate. Isopropylic glycerate has a somewhat lower rotation than the normal propylic compound, but the isobutylic glycerate lies much more nearly on the "main line" of molecular rotatory increase than either the normal or secondary butylic compounds, the rotations of which correspond closely with that of the isopropylic glycerate. It is pointed out that the addition of $CH_2$ to the alkyl group increases the molecular rotation by 6·54 in the case of methylic and ethylic, and of 6·85 in the case of the ethylic and normal propylic glycerates, whilst the increase is only 5·56 in the case of the isopropylic and isobutylic glycerates. These values for $CH_2$ are very similar to those which can be deduced in the case of ethereal salts of tartaric acid, in which, also, the rotatory value of $CH_2$ is less in the case of the iso than of the normal compounds.

In reviewing the rotatory power of these active glyceric ethereal salts in relation to the recently advanced theories of Guye and Crum Brown, they are of opinion that, although in the first three terms of the series, the increase in rotation follows the increase in the weighting of one of the groups attached to the assymmetric carbon atom, yet that by a consideration of the rotatory powers of the higher terms, as well as by a comparison of the rotations of ethylic glycerate and ethylic lactate (the only active lactic ethereal salt hitherto prepared), it is obvious that the molecular rotation is affected by the qualitative nature of the groups as well as by the relative magnitude of their masses.

127. "*Formation of the Ketone 2 : 6-Dimethyl-1-ketohexaphane from Dimethylpimelic Acid.*" By F. Stanley Kipping, Ph.D., D.Sc.

In a recent paper by the author and Mackenzie (*C. S. Trans.*, 1891, 569), it was stated that "when dimethylpimelic acid is heated with phosphoric anhydride at a moderately high temperature, it yields an oil having a strong turpentine-like odour; this reaction will be further investigated by one of us."

Although, on continuing the experiments, only a very small quantity of the oil was obtained in the manner indicated, owing to the formation of resinous products, the investigation was not relinquished, as it seemed probable that the product would prove to be a dimethylketohexamethylene (2 : 6-dimethyl-1-ketohexaphane, *cf. Proc. C. S.*, 1892)—


$$CH_2 \left\langle \begin{matrix} CH_2{\cdot}CHMe \\ CH_2{\cdot}CHMe \end{matrix} \right\rangle CO,$$

the formation of which in this way would be of considerable interest, not only on account of the nature of the product, but also as showing that dicarboxylic acids are capable of undergoing a change similar to that already studied in the case of the fatty acids (*Trans.*, 1890, 532, 980).

Ultimately, by distilling the calcium salt of dimethylpimelic acid with soda lime under reduced pressure, an oil was obtained which, after agitation with soda solution, was distilled, and the portion boiling at about 180° collected separately; this fraction contained a *ketone* of the composition $C_8H_{14}O$ (found, C=76·5, H=11·1 per cent; calculated, C=76·2, H=11·1 per cent), capable of interacting with hydroxylamine, forming a *hydroxime* of the composition $C_8H_{14}$:NOH, crystallising from light petroleum in colourless prisms melting at about 112°; the hydroxime had an odour very similar to that of camphor hydroxime.

The ketone is, in all probability, a dimethylketohexamethylene; it has a peppermint-like odour, which seems to be characteristic of the cyclic ketones of this class, ketopentamethylene (Wislicenus and Hentschel), methylketopentamethylene (Semmler, *Ber.*, xxv., 3517), and suberone, which is probably a methylketohexamethylene (compare Kipping and Perkin, *Trans*, 1891, 217), being all described as having this particular odour.

The publication of this note at present time seems to be desirable in view of the fact that in the last number of the *Berichte* (p. 231) von Baeyer has described a ketone, obtained by the distillation of calcium pimelate with soda lime, which is doubtless a homologue of the compound prepared by the author. The investigation is being continued.

128. "*Note on the Interactions of Alkali-metal Haloids and Lead Haloids and of Alkali-metal Haloids and Bismuth Haloids.*" By Eleanor Field, Assistant Demonstrator in Chemistry, Newnham College, Cambridge.

By boiling potassium or ammonium iodide with lead iodide, chloride, bromide, or fluoride and water in the ratio of 30 parts of the former to 1 part of the lead compound to 75 parts of water, pale yellow needle-like crystals were obtained, having the composition $3PbI_2 \cdot 4KI$ or $3PbI_2 \cdot 4NH_4I$.

By boiling potassium or ammonium chloride, or bromide, with lead iodide and water in the ratio of 6 parts of the former to one part of the lead compound to 50 parts of water, lead iodochloride, PbICl, was obtained.

By boiling potassium or ammonium iodide with lead chloride and water, in the ratio of 1 part alkali of the former to 5 parts lead chloride to 250 parts water, iodochlorides of lead of the composition $PbI_2 \cdot 3PbCl_2$ and $PbI_2 \cdot 5PbCl_2$ were obtained; when lead bromide was used in place of lead iodide, the product was an iodobromide of lead, $PbI_2 \cdot 2PbBr_2$.

These results show that when a large excess of potassium or ammonium iodide is used, the whole of the lead haloid is transformed into iodide, if the lead compound was not iodide to start with, and that the lead iodide thus formed combines with the potassium or ammonium iodide to form a double salt; but that if less alkali-metal haloid be used in proportion to the amount of lead haloid employed, the product contains the halogen of the two haloids, and it is free from alkali-metal. The composition of the products of the interaction depends more on the relative quantities of the interacting haloids than on the nature of the metals and the halogens of the salts employed.

The results obtained by the interactions of the alkali-metal and bismuth haloids differed from those obtained with lead haloids. The compound $BiBrCl_4K_2$ was obtained by dissolving bismuth chloride in solution of potassium bromide used in the ratio $BiCl_3$ : KBr. The compound $BiClBr_4K_2$ was obtained when bismuth bromide was dissolved in solution of potassium chloride in the ratio $BiBr_3$ : KCl. But when bismuth chloride and ammonium bromide interacted in the ratio $BiCl_3 : NH_4Br$, the same substance was obtained as when bismuth bromide interacted with ammonium chloride in the ratio of equal numbers of molecules, viz., $BiCl_3Br_3(NH_4)_3$. This compound is similar to the $SbCl_3Br_3K_3$ obtained by Atkinson (*C. S. Trans.*, 1883, p. 289) by the interaction of antimony and potassium haloids, either in the ratio $SbCl_3 : 3KBr$ or in the ratio $SbBr_3 : 3KCl$.

These results indicate that the composition of the products of change is dependent, not only on the relative masses of the interacting haloids, but also on the nature and relative affinities of the halogens and also of the metals of the interacting haloids.

129. "*An Isomeric Form of Benzylphenylbenzylthiourea.*" By Augustus E. Dixon, M.D.

Phenylthiocarbimide and dibenzylamine interact, forming the compound $C_6H_5N{:}C(SH) \cdot N(C_7H_7)_2$, isomeric with the thiourea $C_7H_7N{:}C(SH) \cdot NC_6H_5 \cdot C_7H_7$ (m. p. 103°), previously obtained by the author (*Trans.*, 1891, 567) from benzylthiocarbimide and benzylaniline: it crystallises in vitreous prisms, insoluble in water, rather sparingly soluble in ether and alcohol, and melting at 145—146° (uncorr.); it is converted by the action of alcoholic ammonia at 100—110° into phenylthiourea and dibenzylamine.

130. "*A New Atomic Diagram and Periodic Table of the Elements.*" By R. M. Deeley.

After a reference to Lothar Meyer's diagram of atomic volumes and Mendeleeff's periodic table of the elements, a diagram is described in which the ordinates are "volume heats" and "volume atoms" instead of atomic volumes; a table of the elements is also given, in which the elements are arranged periodically, in accordance with their positions on the diagram.

The volume heats are obtained by multiplying specific heat by relative density, and the volume atoms by dividing relative density by atomic weight.

### *Hofmann Memorial Lecture.*

An Extra Meeting of the Society will be held on Friday, May 5th, 1893, the anniversary of the death of A. W. von Hofmann, when addresses will be delivered by the Right Hon. Lord Playfair, K.C.B., F.R.S., V.P.C.S.; Sir F. A. Abel, C.B., F.R.S., V.P.C.S.; Dr. W. H. Perkin, F.R.S., V.P.C.S.

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**Experimental Conclusions on the Use of Sand-Filters.**—The result of deliberations carried on in the Imperial Sanitary Office (Kaiserliches Gesundheitsamt), in order to exclude as far as possible the danger of infection from the use of filtered river-water as a supply for towns, may be summed up as follows. Care must be taken that the water used as a supply (river, lake, &c.) must be as far as possible guarded against pollution by human excretions; the mooring of vessels near the spot whence the supply is taken must be especially prevented. A sand-filter does not yield a water absolutely free from germs, and as their efficacy in keeping back micro-organisms, including cholera germs, is limited, the demand made upon the filters must not be increased beyond a certain limit. The speed of filtration must not exceed 100 m.m. (?) hourly. In places where the consumption of water is so great that the above rate of filtration is exceeded remedial measures must be taken. This is effected either by a limitation of the consumption (for which purpose the introduction of water meters in each house is recommended), or by increasing the surface of the filters and installing additional filter-beds. Filters which have become clogged must be removed only so far that a stratum of sand remains of more than 40 c.m. in thickness. The water first run off from a newly built filter, or from one supplied with fresh sand, must not be allowed to flow into the clean water reservoirs or into the mains as it is rich in bacteria. The performance of the filters must be daily checked by bacteriological examination. If greater numbers or unusual species of microbia suddenly appear, the water must be shut off from use and precautions taken. It is even desirable to examine the filtrate from each filter separately. Careful attention to these directions reduces the danger of the entrance of cholera germs into the branch water to a minimum, as it has been lately shown on a large scale by the instance of Altona in comparison with Hamburg.—*Journal Gas-Beleuchtung* and *Chemiker Zeitung.*

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 11, March 13, 1893.

**An Electric Furnace.**—Henri Moissan and Jules Violle.—The arrangement of the furnace cannot be intelligibly described without the two accompanying figures.

**Photographic Properties of the Cerium Salts.**—M. Auguste and Louis Lumiére.—This paper will be inserted in full.

**Metallic Osmium.**—A. Joly and M. Vèzes.—Already inserted.

**Researches on Thallium: Re-determination of its Atomic Weight.**—Charles Lepierre.

**The Zinc and Cadmium Fluorides.**—C. Poulenc.—This paper will appear *in extenso*.

**Determination of Mercury in Dilute Solutions of Sublimate.**—Leo Vignon.—The author takes, *e.g.*, 50 c.c. of a solution of mercuric chloride at one part in a thousand, adding 5 c.c. of pure hydrochloric acid at 22° and 10 c.c. of a clear saturated solution of hydrogen sulphide. The yellow precipitate obtained rapidly turns black; it is filtered through a filter, weighed to one-tenth m.grm., washed, dried, and pressed. It is useful to operate comparatively upon a check filter-paper, through which is filtered a mixture of 50 c.c. distilled water, 5 c.c. HCl, and 10 c.c. $H_2Cl$, which is washed like the former. The weight of this check filter, of the same size and the same paper as the filter containing the precipitate, gives a small corrective coefficient which permits the weight of the mercury sulphide to be determined with more accuracy. In solutions containing one part of mercuric chloride in 10,000, a gravimetric process cannot be applied with accuracy except we can operate upon at least 500 c.c. of solution.

**Alkaline Polyphenolic Phenates.**—M. de Forcrand.—A thermochemical paper which does not admit of useful abstraction.

**Isomerism of the Amidobenzoic Acids.**—Oechsner de Coninck.—The author finds that the *meta*-acid is the most soluble, that the *ortho*- and *para*-acids are less soluble, and in distilled water possess a solubility almost equal respectively.

**The Action of Carbon Monoxide upon Reduced Hæmatine and upon Hæmochromogen.**—H. Bertin-Sans and J. Moitessier.—The authors have obtained a compound of carbon monoxide with hæmatine by setting out directly from reduced hæmatine without having recourse to hæmochromogen.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 5.

**Dibromogallic Triacetic and Tribenzoylic Acids.**—Alex. Bietrix.—The composition of these compounds is $C_6Br_2(OC_2H_3O)_3COOH$ and $C_6Br_2(OC_7H_5O)CO_2H$.

**Researches on the Constitution of the Colouring-Matters of the Rosaniline Group and their Acid Salts.**—A. Rosenstiehl.—Already inserted.

**Identity of the Hydrocarbide, $C_7H_{14}$, derived from Perseite or from Resin with Heptanaphthone (Methylcyclohexane).**—L. Maquenne.—The author establishes the identity of the saturated hydrocarbide, $C_7$, of perseite, that of the essence of resin, that obtained by Markownikoff by saponifying the iodide of the alcohol corresponding to suberone, heptanaphthene, and finally Wreden's toluene hexahydride.

**The Alizarin Formamides.**—M. Prud'homme and C. Rabaut.—The two amidoalizarins are transformed into formamides under the action of formic acid.

**An Electric Furnace.**—M. Saladin.—This paper requires the accompanying figure.

**Preparation of Amylpyrusate.**—L. Simon.—The mixture, in theoretical quantities, of pure pyruvic anhydride and of amylic alcohol is kept for some hours at ebullition under a reduced pressure with an ascending condenser. The condenser is then replaced by a Le Bel apparatus with three bulbs, followed by a descending refrigerator, and distils slowly on the water-bath under a pressure of 10 to 15 m.m. There passes over first a little water and then amylic ether. The yield is theoretical.

**A Reaction of Cupric Salts.**—E. Lenoble.—If into the solution of a cupric salt we pour a solution of double mercury and potassium iodide, we obtain a fine bright red precipitate, whilst a certain quantity of iodine is set free and colours the liquid brown. The precipitate seems to be a compound of cuprous iodide and mercuric iodide

**Production of Mucic Acid (Hexabepic Acid) by the Oxidation of Gum-Arabic.**—E. Maumené.—Not suitable for reaction.

**On Guyacol.**—A. Béhal and E. Choay.—The guyacols of commerce are essentially variable products, their boiling-points ranging from 200° to 215°. None of them contains more than 50 per cent of definite guyacol, the rest consisting chiefly of cresylol and cresol. Pure guyacol is a white, crystalline solid, fusible at 28·5° and boiling at 205·1°.

**On Asboline (Pyrocatechine and Homopyrocatechine).**—MM. Béhal and Desvignes.

**Analysis of Officinal Creosotes.**—A. Béhal and E. Choay.—These two papers are not suitable for abstraction.

**Chemical Conditions of the Action of Diastase.**—Dr. Jean Effront.—The author finds the nitrogenous residue from the manufacture of glucose, and studies the behaviour of its constituents with asparagine, aluminium, and phosphoric acid.

**On Potassium and Ammonium Tetrachromates.**—G. Wyrouboff.—M. Schmidt's note in the Berlin *Berichte* has been anticipated by the author twelve years ago.

## MEETINGS FOR THE WEEK.

FRIDAY, April 7th.—Geologists' Association, 8.
— Quekett Club, 8.

THE CHEMICAL NEWS.

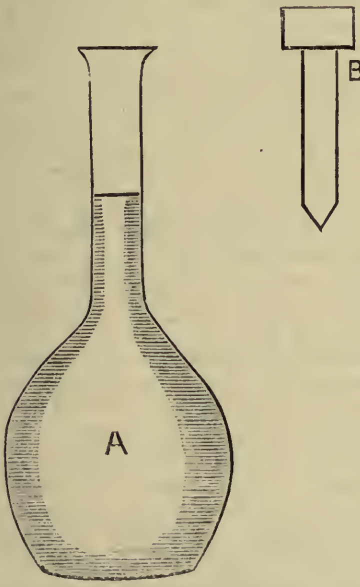
Vol. LXVII., No. 1741.

## ON AN IMPROVED STOPPER OF MEASURING FLASKS FOR MEASURING LIQUIDS QUICKLY.

By ALEX F. REID.

During the last year I have had several articles in the Chemical News (vol. lxv., pp. 68, 125; vol. lxvi., p. 166) on improvements in analytical apparatus. These improvements were effected chiefly to save time in the analytical operations of the laboratory. They are in constant use, and by their means much more work is got through with quite as accurate results. I refer to their use in the laboratory of the Cassel Gold Extracting Company, Ltd., of Glasgow, for the testing of potassium cyanide.

There is still a simple contrivance which I find of much use in measuring out water in litre or other flasks. It consists of a wooden or indiarubber plug, B, which fits loosely into the neck of the flask, A, and of such a size that the part of it that goes into the flask has the same volume as the part of the flask above the mark. The flask is first filled up past the graduation line with water. The stopper is inserted and then pulled out. The surplus water runs out, and the right quantity remains. The stopper has a tapered point to admit of it being put in quickly, and also to allow the water to run off readily when it is being withdrawn.



Bonshaw, Stewarton, N.B.

Royal Institution.—On Saturday, April 15, Mr. James Swinburne, M.Inst.E.E., will begin a course of three lectures on "Some Applications of Electricity to Chemistry." The Friday Evening Meetings will be resumed on April 14, when Sir William H. Flower will deliver a discourse on "Seals."

## ON ZINC AND CADMIUM FLUORIDES.

By C. POULENC.

Marignac has shown that zinc fluoride, $ZnFl,4H_2O$, loses its water at 100° and appears in the form of a white amorphous powder. We have succeeded in preparing it anhydrous and crystalline by applying the methods which we have formerly indicated.

1. *Action of Anhydrous Hydrofluoric Acid upon Zinc.*—Gaseous hydrofluoric acid does not attack zinc except above a dull red heat. Zinc fluoride is formed and hydrogen escapes. For the platinum tube we have hitherto made use of a tube of retort-coke to avoid the formation of an alloy of platinum and zinc.

2. *Action of Anhydrous Hydrofluoric Acid upon Melted Zinc Chloride.*—Melted zinc chloride is decomposed in the cold by vapours of hydrofluoric acid, but the temperature must be raised to 800° or 900° in order to obtain anhydrous crystalline zinc fluoride. Under such conditions we observe that the sides of the platinum tube are coated with fine colourless transparent needles of volatilised fluoride, and that the contents of the platinum boat likewise present the aspect of a crystalline mass.

3. *Action of Anhydrous Hydrofluoric Acid upon Zinc Oxide and Zinc Hydroxide.*—These two substances equally give rise to anhydrous crystalline zinc fluoride if heated below redness in a current of gaseous hydrofluoric acid.

*Properties.*—Zinc fluoride appears in the form of fine transparent colourless needles. They polarise light strongly, and belong apparently to the monoclinar or triclinar system. The specific gravity at 15° is 4·84. It is sparingly soluble in cold water, but its solubility increases with the temperature. It is insoluble in alcohol at 95°. Hydrochloric, nitric, and sulphuric acids dissolve it at the temperature of ebullition. Zinc fluoride is reduced at a red heat by hydrogen, which carries away vapours of zinc. If ignited in the air it is converted into zinc oxide. Watery vapour produces the same reaction at a red heat. Gaseous hydrogen sulphide passing over heated zinc fluoride decomposes it into zinc sulphide and hydrofluoric acid. Gaseous hydrochloric acid under the same conditions yields melted zinc chloride. If melted with alkaline carbonates there is formation of zinc oxide and an alkaline fluoride.

*Cadmium Fluoride.*—If we evaporate a hydrofluoric solution of cadmium fluoride we obtain, according to Berzelius, a crystalline fluoride, adhering very strongly to the sides of the vessel in which it has been formed. This compound, which we have dried in the stove at 120°, still retains a small quantity of water, and does not correspond to a well-defined formula. We have succeeded in preparing anhydrous cadmium fluoride by the same procedures which yielded zinc fluoride.

1. *Action of Anhydrous Hydrofluoric Acid upon Cadmium.*—Cadmium is attacked more readily than zinc and at a lower temperature. The experiment should be made in a tube of retort coke to avoid the formation of metallic alloys.

*Action of Anhydrous Hydrofluoric Acid upon Melted Cadmium Chloride.*—Cadmium chloride, recently melted and pulverised, can scarcely be decomposed at the ordinary temperature by gaseous hydrofluoric acid. A rise of temperature facilitates the reaction, but never renders it complete. The cadmium fluoride formed remains in the boat as a colourless transparent melted mass, whilst the undecomposed cadmium chloride is volatilised.

*Action of Anhydrous Hydrofluoric Acid upon Cadmium Oxide.*—The acid decomposes it at a red heat, producing thus melted cadmium fluoride. But to whatever temperature we raise the fluoride (1200°) we never observe a trace of volatilisation. This latter character differentiates it distinctly from zinc fluoride.

The action of anhydrous hydrofluoric acid obtained by the moist way gives rise to the same compound as above, *Properties.*—Cadmium fluoride, if it has been raised to a high temperature, is a colourless, translucid mass, which crumbles into small fragments with a conchoidal fracture. Its sp. gr. is 6·64. It is very soluble in water, but insoluble in alcohol at 95°. Hydrochloric, nitric, and sulphuric acids dissolve it at ebullition. The sulphuric solution, if evaporated on the sand-bath, deposits anhydrous crystalline cadmium sulphate. This compound, which the author believes he has been the first to make known, is formed of small, colourless, very brilliant prisms, which gradually tarnish on exposure to air.

Cadmium fluoride is reduced by hydrogen at redness. If ignited in the air it is totally converted into cadmium oxide. Watery vapour at red heat gives the same reaction.

Hydrogen sulphide, if passed over cadmium fluoride, slightly heated, decomposes it into yellow cadmium sulphide and hydrofluoric acid. Gaseous hydrochloric acid under the same conditions yields cadmium chloride. This reaction, which takes place more easily than the inverse reaction, explains why we have never obtained the complete conversion of cadmium chloride into fluoride.

Melted alkaline carbonates decompose it into cadmium oxide and an alkaline fluoride.—*Comptes Rendus*, cxvi., p. 581.

## IN MEMORY OF C. W. SCHEELE.

On December 9th last, the 150th anniversary of the birth of Scheele, A. E. von Nordenskiöld, the celebrated Polar explorer, published a collected edition of his correspondence and laboratory notes. From a notice of this work from the pen of E. von Meyer (*Journ. fur Prakt. Chemie*) we make the following excerpts:—

"Although Scheele is sufficiently known as a promoter of analytical chemistry it was little imagined that he had in the acutest manner utilised his observations for the development of quantitative methods. We now learn that he was the first to carry out the separation of iron and manganese by means of acetic acid. He further made use of the alkalies for opening up silicates; he recognised the difference between soluble and insoluble silica, and in 1772 paved the way the discovery of which has been mistakenly credited to Bergman. With the reactions of the salts of magnesium, copper, and mercury he showed himself acquainted to an extent shared by none of his contemporaries. He was aware that silver chloride is soluble in hydrochloric acid but insoluble in nitric acid, and he utilised the flame colourations of the salts of potassium and sodium.

"He has hitherto been acknowledged along with Priestley as the discoverer of oxygen, though Priestley is said to have first observed the gas a year earlier than Scheele. But from his laboratory notes and correspondence it now appears with full certainty that Scheele had obtained oxygen by various methods, and had described it accurately in 1771 or in the beginning of 1772. He named it first "vitriolic air," subsequently "fire air" (*aer purus, aer vitalis*). He prepared it then from nitrates (saltpetre, magnesium nitrate), from manganese ore and arsenic acid or sulphuric acid, from mercuric oxide, silver carbonate (along with carbonic acid), and from gold oxide. This fundamental discovery, from which a new epoch in chemical science must be dated, slept for some years and was made public in 1774 by Priestley, though in a much less complete manner.

"From the new work we learn to recognise Scheele, even in his earlier years, as a master in the treatment of gases. We find that as far back as 1770 he recognised nitrogen, hydrogen sulphide, hydrogen chloride, ammonia, and nitric oxide as distinct gases, and studied their properties. He was the first observer of liquid hydrogen sulphide and of chamber crystals.

"In his works we repeatedly find startling communications on the different stages of oxidation of the metals, especially iron, copper, and mercury, which he, of course, sought to explain on the phlogistic hypothesis."

## THE ABSORPTION OF FREE NITROGEN BY PLANTS.

(Concluded from p. 149).

The concluding experiments of M. Boussingault, on which he relies for the refutation of his own former conclusions, were, as we have already stated, made under such conditions that correct results could not be expected. He effected his cultivations in closed globes of the capacity of 6 to 10 litres!

As M. Ville justifiably asked, what can be expected of plants under such conditions?

A still more unfortunate departure from the natural conditions of plant-life was the very limited quantity of the sand used as soil. M. Boussingault used only 60 or 120 grms. for each experiment, a quantity about sufficient to fill the shell of a nut; and in such tiny lots of soil he sowed peas and haricot beans. Now, if a plant is to flourish, its roots must find in the soil a space adequate to the development which it should take. This condition is systematically violated in M. Boussingault's experiments, made in the years 1851 and 1852.

Another objection is, that to this reduced quantity of sand M. Boussingault added, as an inorganic manure, from 1 grm. to 10 grms. of the ash of farmyard manure. As such ash contains about 50 per cent of alkaline salts, the proportion of alkali was excessive to such an extent as to be injurious to plant-life.

Finally, the seeds were sown at a wrong season of the year. Every farmer and every gardener knows that this is a most serious error. A plant cultivated at the wrong time never takes a complete or normal development. For instance, wheat sown in May or June yields merely a grassy tuft. Colza sown in April flowers immediately after germination. Hence it could only be expected that the results of the experiments would be negative—as it was actually the case. To argue from results obtained under such unnatural conditions to what takes place in normal growth is eminently unscientific.

How decidedly contradictory are the conclusions which M. Boussingault has maintained at different times we need merely refer to his memoirs published in the *Comptes Rendus*.

In 1838 (*Comptes Rendus*, vi., p. 129) he asserts that the nitrogen of the air is absorbed by plants, and a report drawn up by M. Dumas and read before the Academy of Sciences formally consecrated this declaration.

In 1854 he asserts precisely the contrary (*Comptes Rendus*, xxxviii., p. 580).

In 1854 he announces that plants flourish in a confined atmosphere as well as in the open air (*Comptes Rendus*, 1854, xxxix., p. 603).

In 1859 he demonstrates just the opposite, *i.e.*, that vegetation is more flourishing in the open air than in a limited confined atmosphere (*Comptes Rendus*, 1857, vol. xlviii., pp. 310 and 312).

In 1855 he states that plants cultivated with an addition of saltpetre live only from the nitrogen of this salt, and do not derive any from the air (*Comptes Rendus*, 1855, xli., p. 485).

In 1859 he recognises that a plant cultivated with the aid of saltpetre derives nitrogen from the air (*Comptes Rendus*, 1859, xlviii., 312).

Lastly, in 1866 he does not deny, but he does not distinctly affirm; he recognises that in the open air plants cultivated in ignited sand absorb *a little nitrogen* supplied by the ammonia of the atmosphere (*Revue des Cours Scientifiques*, 1865—1866, sixth issue, p. 97).

It is superabundantly plain that this admission is quite inadequate. The nitrogen present in the atmosphere in the state of ammonia, if entirely absorbed, would fall far short of meeting the wants of vegetation. This fact is the reason why some additional source has been sought for. Hence, if plants cannot utilise the free nitrogen of the atmosphere, we must admit that there exists in the soil, in the water, or in the atmosphere some abundant source of nitrogen which escapes our analysis. It is surely less rational to admit the existence of such an unknown source than to recognise the absorption of free nitrogen by plants.

In answer to the question how is such free nitrogen absorbed? we have positive facts to advance. Since the researches of Boussingault were effected, it has been established that the small nodules which we find in such abundance on the roots of beans and other leguminous plants are in reality minute chemical laboratories, in which the fixation of the atmospheric nitrogen is effected. The agents there at work are certain microbia. This fact explains the fertilising action of crops of clover when ploughed into the soil, as M. Ville has so ably and thoroughly expounded in his treatise "The Perplexed Farmer" (Longmans and Co.), or in his larger work on "Artificial Manures."

But we now find that not alone leguminous plants, such as clover and peas, but other kinds of vegetation, though not provided with root nodules, are able to absorb and fix free nitrogen. This M. Ville has shown analytically. If experimental plants are cultivated under normal conditions, the crop is found to contain an excess of combined nitrogen over and above what can be derived from the soil,—including the manures,—from the ammonia and nitric oxide of the air, and from ammoniacal salts existing in solution in the water. The patience and perseverance with which M. Ville has insisted on these phenomena demand the fullest recognition.

## THE ANALYSIS OF IRON AND STEEL.[*]

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 150.)

*Phosphorus.*— The methods generally employed for the determination of this element consist in the conversion of the phosphorus into phosphoric acid by means of an oxidising agent, usually nitric acid, and the subsequent precipitation either as ammonium magnesium phosphate or ammonium phospho-molybdate. Chemists differ considerably in opinion as to which of the methods is the better. We are of opinion that the last named, or the "molybdate" method, as it is termed, is preferable, and for this reason it will be the only one we shall describe. The process requires the employment of a solution of molybdate of ammonia, which is prepared by dissolving 60 grms. of the crystals in water, making up to a volume occupying a litre, and adding 50 c.c. of ammonia (sp. gr. 0·88), and a slight excess of ammonium nitrate. The solution is allowed to stand for two or three days, and is then decanted from any precipitate formed.

For the analysis 4 grms. of the sample (with very pure irons it is sometimes necessary to use as much as 10 grms.—with phshoric irons 2 grms., or even 1 grm. is quite sufficient) are placed in a porcelain dish, covered with 60 c.c. of nitro-hydrochloric acid, and heated at a gentle temperature until the iron is dissolved. The resulting solution is now carefully evaporated to dryness and heated highly. This is continued until the whole residue becomes black. Upon cooling, the residue is moistened with 60 c.c. of hydrochloric acid, the solution heated and taken to dryness in order that complete separation of the silica shall be ensured. The whole is then re-moistened with a small quantity of hydrochloric acid and heated until solution is effected. To the resulting liquid five times its volume of hot distilled water is added, and the silica separated by filtration. The filtrate contains the phosphoric acid, but before it can be precipitated a large portion of the hydrochloric acid must be got rid of, and the volume considerably lessened. This is effected by adding nitric acid (sp. gr. 1·42) and evaporating to a thick syrupy condition, which operation is repeated until it is judged from the colour of the solution (which becomes lighter as the quantity diminishes) that the greater portion of the hydrochloric acid has been expelled. Finally, to the syrupy mass sufficient nitric acid is added to cause it to flow freely in the precipitating vessel, and 50 c.c. of the ammonium molybdate solution is then added. The liquids are thoroughly assimilated by brisk agitation, and the vessel is set aside to stand for a few moments in a warm place. The next step is to ascertain, as far as can be judged by smell, whether the solution is of the right degree of acidity, so that while, on the one hand, there is sufficient acid present to prevent an excess of ammonium molybdate coming down along with the phosphorus, there is not, on the other hand, sufficient to prevent the complete precipitation of the phosphorus. If it is found that the solution is excessively acid, ammonia (sp. gr. 0·88) is cautiously added, the vessel agitated briskly to dissolve the precipitated iron, and allowed to stand for a few moments after each fresh addition, until only slightly so. We have ascertained that the molybdate precipitate is slightly soluble in dilute nitric acid. If the solution is ammoniacal, nitric acid (sp. gr. 1·42) is added until it is slightly acid.

(A solution of phosphate of iron was made, and mixed with excess of perchloride of iron. 100 c.c. of this solution contained 0·01152 grm. phosphorus. For the experiments 100 c.c. of the solution was poured into a tube 100 c.c. Burette divided into 200 parts, provided with an Erdman's float, so that the number of c.c. to be used could be accurately run out. *Expt.* 1.—To 25 c.c. solution excess of ammonia was added, then acidified with nitric acid, boiled, 8 c.c. molybdate solution added, and sufficient nitric acid until precipitation. Set aside on sand-bath 26 minutes. Mean of five trials, phosphorus found, 0·002868 grm.; phosphorus in solution, 0·002880 grm. *Expt.* 2.—25 c.c. solution as above was mixed with 12 c.c. molybdate solution, to ascertain whether excess of molybdate would interfere with the accuracy of the process. Phosphorus found, 0·003085 grm. *Expt.* 3.—10 c.c. molybdate solution added to 25 c.c. phosphorus solution afforded 0·002880 grm. phosphorus. *Expt.* 4.—16 c.c. molybdate solution added to 25 c.c. phosphorus solution, on four trials, afforded 0·003378 grm. phosphorus, *Expt.* 5.—12 c.c. molybdate solution added to 25 c.c. phosphorus solution, along with an excess of nitric acid, afforded 0·001369 grm. phosphorus. *Expt.* 6.—12 c.c. molybdate solution, added to 25 c.c. phsphorus solution, 7 c.c. excess of nitric acid Phosphorus found, 0·00271 grm. *Expt.* 7.—As above, but 14 c.c. excess of nitric acid used. Phosphorus found, 0·001450 grm. (The experiments 6 and 7, when set aside for many hours, gave no further precipitate.) *Expt.* 8.—It was thought that in experiments 2 and 4, with 12 c.c. and 16 c.c. molybdate solution, a shorter time might suffice for the precipitation of the phosphorus. Accordingly, experiments 2 and 4 were repeated, but only allowed to stand 12 minutes. Phosphorus found, 0·002958 grm., experiment 2 (two trials) Experiment 4 repeated with 16 c.c. molybdate solution, and a slight excess of nitric acid for 12 minutes. Phosphorus found, 0·00295 grm. *Expt.* 9.—16 c.c. molybdate solution to 25 c.c. phosphorus; solution boiled, after precipitation of phosphorus set aside, for 15 minutes. Phosphorus found, 0·004254 grm. The foregoing experiments show that great caution must be exercised throughout the whole process.)

After the right degree of acidity is got, the solution is

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[*] From *Industries*, February 4, 1893.

allowed to stand in a warm place until the yellow precipitate of phospho-molybdate has settled at the bottom of the containing vessel and the supernatant liquid has become clear. The precipitate is then collected on a tared Swedish filter-paper, a dilute solution of nitric acid of 1 acid to 10 water being employed to throw it on. The filter and contents should be washed six times with the dilute nitric acid solution, and then removed to a water-oven, dried, and re-weighed. The increase in weight is due, as is obvious, to phospho-molybdate, which contains 1·66 per cent of phosphorus.

Arsenic is precipitated as arsenic-ammonium-molybdate, by ammonium-molybdate, and, as the metal is sometimes present in iron and steel, a portion of it would be thrown down in conjunction with the phosphorus. This may be estimated by the knowh methods, or by the method of Stead. Arsenic may be eliminated by previous treatment with sulphuretted hydrogen.

Some chemists recommend, with a view of saving time, that the evaporation to dryness of the nitro-hydrochloric acid solution, as above described, be dispensed with, and that it be evaporated until it acquires a syrupy condition only, adding then simply hydrochloric acid, heating to boiling, filtering, &c., and determining the phosphorus in the filtrate as above. We have tried this method, which undoubtedly considerably shortens the operation, but we have always obtained lower percentages than those obtained by the method above described. The method is only applicable to steels containing little or no silicon. In pig-irons the silicon interferes with the accuracy of the results obtained by this method.

(To be continued).

## TECHNICAL ESTIMATION OF MANGANESE IN ORES.

By ALBERT H. LOW.

Prepare the following solutions:—A standardised solution of potassium permanganate, approximately one-tenth normal. A solution of oxalic acid containing about 11·46 grms. of $C_2O_4H_2,2H_2O$ per litre. Determine the exact strength of this solution by titrating with the permanganate in the presence of hot dilute sulphuric acid in the usual manner, and then calculate its value in manganese on the basis that $C_2O_4H_2,2H_2O = Mn$. It will be found 1 c.c. will equal about 0·005 grm. of Mn, or about 1 per cent when 0·5 grm. of ore is taken for analysis. A saturated solution of bromine in cold water. Always keep an excess of bromine in the bottle. Under the conditions to be described, 25 c.c. of this solution will precipitate about 35 per cent of manganese.

### *Method of Analysis.*

Treat 0·5 grm. of the ore in a 16-ounce flask with whatever acids are necessary to decompose it. Usually 5 to 10 c.c. of hydrochloric acid or aqua regia are sufficient. Boil until the free acid is nearly gone. This may be accomplished in two or three minutes by manipulating the flask over a naked flame. Dilute with about 75 c.c. of hot water, and add an excess of ZnO. Boil to effect complete neutralisation of the acid. Now add an excess of the bromine solution (usually 25 c.c., never more than 50 c.c.), and boil for a minute or two until the excess is expelled, as indicated by the disappearance of the red fumes. An excess of ZnO should still be observed in the bottom of the flask. Filter, using a filter about 5 inches in diameter, and wash flask and precipitate several times with hot water. Place the washed precipitate, together with the filter, back in the flask, and add a sufficient amount, say 50 c.c., of dilute sulphuric acid (1 to 9). Run into this mixture, from a burette, what is judged to be an excess of the oxalic acid solution, remembering that 1 c.c. equals about 1 per cent of Mn. Heat the mixture to boiling, and then, if necessary, add more oxalic acid, so as to effect complete solution of the precipitate. Now dilute somewhat with hot water, and titrate the excess of oxalic acid with the permanganate solution. The number of c.c. of oxalic acid actually consumed by the $MnO_2$ is thus arrived at, from which the percentage of manganese is then calculated. The entire analysis need not occupy more than twenty minutes. None of the ordinary constituents of ores interfere with the method, and the results obtained are very satisfactory.

Of course other reducing agents can be used in place of the oxalic acid solution. When the latter is not at hand a weighed amount of the double sulphate of iron and ammonium will be found convenient.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

## NOTE ON THE DETECTION OF CHLORINE, BROMINE, AND IODINE IN THE SAME MIXTURE.

By JOSEPH TORREY.

I read Mr. Kebler's note on the above subject in the *Journal of Applied Chemistry* (October, 1892) with much interest. The problem is one of the most difficult in qualitative analysis. For an experienced chemist it is not so difficult, but the point is to find a method that can be used by students.

The object of this note is to describe some very slight modifications of Dr. Hart's method, which in my experience have made it a little more convenient. The general procedure was given by Mr. Kebler, and need not be repeated here. I have found no occasion to modify the details so far as the evolution successively of the chlorine, bromine, and iodine is concerned; but the bulb-tube arrangement figured in the original description, and the methods for detecting the halogens as they come off, have been modified as follows:—

Instead of the bulb apparatus originally described, I use a small tube having one small bulb blown on it, the tube being bent slightly away from the perpendicular about half an inch above where it leaves the cork. Above the bulb there should be about half an inch of tube left. The flask containing the mixture to be analysed is charged with ferric sulphate as usual, and the iodine evolved; a small piece of starch-paper is held in the steam as it emerges from the tube, and any iodine speedily shows itself. When the iodine has all been expelled by boiling, as will be seen by the negative indication of the starch-paper, a crystal of potassium permanganate is added, and, on heating, the bromine is evolved. For detecting it I use iodised starch-paper in the same way as starch-paper was previously used, and any bromine is easily detected. The boiling is continued until all bromine is gone, when the chlorine is detected as usual.

The only points where care is necessary in giving this process to students are the following:—

1. Care must be taken that very small quantities of substance are used. The merest trace of any one of the halogens will be detected with certainty, and large quantities only waste time and fill the laboratory with undesirable fumes,
2. The boiling must be continued till no trace of bromine can be detected before testing for chlorine. The boiling must be quite brisk, or bromine will be mechanically held back.

For delicacy, rapidity, and certainty I have yet to find the equal of this process. With a reasonable amount of care the character of the mixture is practically immaterial. In the original paper it appeared from the published experiments (in which I suppose I had a hand) that a large quantity of bromine masked the iodine test. I have not found the same effect to be present when the starch-paper is used to detect the iodine.

During the last two years of the Summer School of Chemistry at Harvard University I have had many experiments made with mixtures of very varying proportions, and have never yet met with any but favourable and satisfactory results.

Last summer some work was done toward seeing whether the process could not be turned to account quantitatively. The outlook was encouraging, but the time was too short to accomplish enough to make it certain. I hope the work may be continued the coming summer.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

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## A NEW PROCESS FOR THE MANUFACTURE OF MANGANESE ON THE COMMERCIAL SCALE.*

By WM. H. GREENE and WM. H. WAHL.

Within a few years manganese has assumed considerable importance as a constituent of several alloys, and the purest manganese of commerce as well as the richest ferro-manganese have been unsatisfactory for the preparation of these alloys by reason of the high proportion of carbon invariably present.

About two years ago we were induced to undertake the search of a process for the manufacture, on a commercial scale, of metallic manganese that would contain a minimum of detrimental impurities and be absolutely free from carbon. Before describing the process which we have elaborated, we will review briefly the history of the element.

About 1774, Scheele and Bergmann demonstrated that the metallic radical of manganese dioxide is different from iron, and John (*Gehlen's Jour. Chem. Phys.*, iii., 452) isolated the new element by heating a mixture of manganese carbonate and oil, powdering the resulting mass, again mixing it with oil, and strongly heating in a brasqued crucible.

St. Claire Deville (*Ann. de Chemie et de Physique* [3], xlvi., 182) modified this process as follows: he reduced pure artificially-prepared dioxide to red oxide; mixed this with sugar charcoal in insufficient quantity to reduce the entire quantity of oxide, and heated the mixture in a lime crucible to the highest temperature of a wind furnace.

Brunner (*Pogg. Annalen*, ci., 264) heated manganese fluoride, or a mixture of manganese chloride and calcium fluoride, with sodium in clay crucibles.

Giles (*Philosoph. Mag.* [4], xxiv., 328) prepared a manganese amalgam by the action of sodium amalgam on a concentrated solution of manganese chloride, and expelled the mercury by heating in a current of hydrogen, thereby obtaining pulverulent manganese.

Bunsen (*Pogg. Annalen*, xci., 619) obtained deposits of metallic manganese by electrolysing a concentrated solution of manganous chloride.

The first attempt to produce the metal in considerable quantity appears to have been made by Hugo Tamm (Chem. News, xxvi., 111), who, in 1872, published the results of experiments made on certain modifications of John's method. Native dioxide was reduced by heating with powdered charcoal and oil in the presence of siliceous and fluorspar fluxes in graphite crucibles.

The problem presented to us was the reduction of a native oxide of manganese, for it is apparent that the expense of preparation of halogen compounds of the metal, and their subsequent reduction, would preclude the possibility of applying such a method to manufacturing on a commercial scale.

At the outset of our work it became evident that the first step in the process would be the purification of the ore from iron, which would inevitably be reduced in the reduction of the manganese, and could not then be removed from the metal. Magnetic separation appeared to be the cheapest and most effective method, and we made exhaustive experiments in this direction, the ore being treated in all states of division and in all conditions of oxidation, between that of the natural ore and that in which the manganese was reduced to manganese monoxide and the iron to metallic iron. We were compelled to abandon the method entirely, because the iron and manganese are so intimately associated in the ore that no satisfactory separation can be accomplished by the magnet.

We then tried various electro-chemical methods, the ore being made the anode of baths containing sodium chloride solution, ferrous sulphate, dilute sulphuric acid, &c. By such means a certain proportion of the iron may be removed, but the separation is slow, and is far from complete when the manganese oxides begins to be attacked.

Convinced that only a chemical method would answer the purpose, we found after a number of experiments that nearly all the iron can be removed from rich manganese ores by digesting the pulverised ore with about 30 per cent sulphuric acid near the boiling point, while the manganese is practically unattacked. As an illustration of the effectiveness of the process, we may state that in a few hours the percentage of iron may thus be reduced from five or six to a few tenths, with a loss of not more than one per cent of the manganese present. The copperas that may be obtained by treatment of the waste acid with scrap iron will pay the cost of purification of the ore.

The reduction of the ore has been a perplexing problem. While it has never been denied that reduction by carbon in any form yields a metal containing a considerable proportion of the reducing agent, the literature of the subject indicated that this combined carbon might be removed by fusion of the metal under a layer of manganous carbonate or manganous oxide. Thus, Tamm (Chemical News, xxvi., p. 111) claims to have obtained from a pyrolusite containing 79·5 per cent Mn and 6·5 per cent $F_2O_3$, a metal containing—

| | |
|---|---|
| Mn .. .. .. .. .. .. | 96·90 |
| Fe .. .. .. .. .. .. | 1·05 |
| C .. .. .. .. .. .. | 0·95 |
| Other elements .. .. | 1·10 |

and by refining this with manganese carbonate we have raised the proportion of manganese to 99·91 per cent. Other investigators admit the presence of more carbon in the product, but still claim that it may be removed by treatment with manganese carbonate. Our experiments show that the reduction by carbon takes place readily, and only after frequently repeated experiments, in which the proportions of oxide and carbon and the character and proportions of flux employed were varied through wide ranges, did we come to the conclusion that it is impossible by this method to prepare a metal containing less than about 6 per cent of carbon, and that it is equally impossible by fusion with an oxidising agent to remove carbon thus combined with mangangese. The results of experiments recently published by Guntz (*Comptes Rendus*, cxiv., p. 115) explain clearly these phenomena. He finds that carbon monoxide is rapidly decomposed by manganese at a red heat, carbon and manganese monoxide being formed. It can then be readily understood why carbon free manganese cannot be made in the electrical furnaces nor in graphite crucibles.

From all these facts we have been led to infer that the reduction of manganous oxide by carbon yields not manganese, but a definite carbide having the composition

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* Read before the Chemical Section of the Franklin Institute, March, 1893.

$Mn_3C$. We propose investigating this point in the future.

It then became evident that the problem could only be solved by a reduction taking place in the entire absence of carbon. Tentative experiments having given no encouragement to hope that an electrolytic method depending on the decomposition of fused baths of manganese chloride or manganese fluorides mixed with other chlorides and fluorides could be devised, the only alternative became a purely chemical process, the details of which were worked out during the progress of the laboratory work. The importance of these details will become apparent as we describe the steps of our process.

The pulverised manganese ore purified from iron, or containing less than one per cent iron, is exposed to the action of reducing gases at a temperature approximating redness. All the manganese is thus converted into greenish grey manganese monoxide, which must be allowed to cool out of contact with air to prevent oxidation to red manganosomanganic oxide.

The monoxide is then mixed with about 18 per cent of its weight of granulated aluminium and a suitable flux and the mixture is heated to a temperature near the melting point of cast iron in magnesite crucibles. The flux may be siliceous or a mixture of lime and fluorides, or lime alone. As soon as the temperature of reaction is attained the mass promptly fuses, and must be poured from the crucible while at its maximum temperature. While the character of the flux has little influence on the reaction, it has important relation to the yield and quality of the metal obtained. A siliceous flux naturally occasions the introduction into the manganese of a certain proportion of silicon. If the flux be too fusible a quantity of the aluminium may rise to the surface and escape the reaction. A mixture of lime and fluorspar has given us the best results in crucible operations.

Theoretically one part of aluminium should yield three parts of manganese; the best results we have obtained on the small scale, producing several pounds of manganese at one operation, have given us two and eight-tenths parts, or 93 per cent of the theoretical yield, and our average yield has been about 87 per cent. With aluminium at its present price we therefore estimate that the absolute cost of producing carbon free manganese containing, Mn 96 to 97 per cent, Fe and Si each one to two per cent, by our process, will be within thirty-five cents a pound, this estimate including all expenses.

On the large scale we purpose conducting the operation on a magnesite lined hearth, reducing gases being in slight excess. By this means we believe that the manganese will be retained in the state of lowest oxide until the temperature of reaction is reached, and that the prompt fusion of the flux at this stage will protect the manganese formed from contamination by carbon from the flame.

We may mention, in conclusion, that having experienced considerable difficulty in obtaining and preparing magnesite crucibles, we adopted the expedient of lining plumbago crucibles with a stiff paste of calcined magnesite. When properly prepared, these linings do not crack on drying, and do not shrink from the plumbago walls. After thorough drying, the crucibles are ready for use, and we have found the linings very serviceable, not only for the preparation of manganese, but in other metallurgical work in which siliceous or plumbago crucibles were from any cause objectionable.

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**On Solubilities.**—A. Etard.—Gay-Lussac represented solubility at saturation graphically by plotting out the temperatures as abscissæ and the variable quantities of a salt which 100 parts of water can dissolve as ordinates. The author takes the ordinates as proportional not to the quantity of the salt dissolved by the fixed and arbitrary amount of 100 parts of water, but to the weight of the salt contained in 100 parts of the saturated solution.—*Bulletin de la Société Chimique de Paris*, No. 3.

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## GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR, LL.D., F.R.S., F.R.S.E., and J. B. HENDERSON.

(Concluded from p. 152).

The above report includes all the experiments that we made, whether successes or the reverse. On the other hand, we have to confess that the displacement of the reduction tube was not in all cases exactly equal to that of its tare. Originally this was the case to within less than 0·4 c.c., but the reduction tube had to be renewed twice, and the two new tubes were simply made on the model of the original one, and then weighed against the original tare without readjustment of the latter. Hence, before going any further, we had better calculate the maximum uncertainty which our oxygen weights are infected with on this account. The tare apparatus displaced 167·5 grms. of water, and as we took great care to make the new reduction tube as nearly as possible identical with the original one, it is almost impossible to assume that their outer volumes differed by more than, let us say, one-fifth of the value, or by 33·5 c.c. We will adopt this number as representing a limit-value for the unknown difference. Now, supposing the temperature and pressure of the atmosphere in the morning, when the first weighings were made, were $t'^{\circ}$ and P′ m.m., and the corresponding values at the second weighings were $t''=t'+\theta$ and $P''=P'+p$ m.m. (The latter values are given above, the former are before us in our Journal, but we do not deem it necessary to transcribe them here). Then we have for the greatest possible value of the error in a given experiment the approximate expression—

$$\pm 33·5 \times \delta \left(\frac{P}{P} - \frac{\theta}{T}\right),$$

where $\delta$ stands for the weight of 1 c.c. of air in m.grms. as it was in the morning, and T for 273 + the temperature as it was in the evening. For the present purpose $\delta$ may be put down at the constant value of 1·227, and P at 760 m.m. We have calculated the corrections for the several experiments recorded, and found that the correction attains its maximum in the case of Experiment 5, for which it is $= -0·49$ m.grm.; next after it comes Experiment 9 with $-0·19$; then Experiment 6 with $-0·16$. For all the rest, the values found were considerably less. Hence this error may be neglected. In the following Table the first column gives the number of the experiment; the second, the values $h_0 : S_0$ found; the third, the value $x$ calculated therefrom for the atomic weight of hydrogen; the fourth, as "residuals" the differences $x = x_0$, where $x_0$ is the adopted "mean value":—

*Summary of Results.*

| No. | | $h_0 : S_0$. | $x=8\ (h_0 : S_0)$. | Residuals. $x_0=1·00913$. |
|---|---|---|---|---|
| 6 | .. .. | 0·125521 | (1·00417) | −0·00496 |
| 10 | .. .. | 0·125912 | 1·00730 | −0·00183 |
| 12 | .. .. | 0·125959 | 1·00768 | −0·00145 |
| 9 | .. .. | 0·126021 | 1·00817 | −0·00096 |
| 3 | .. .. | 0·126040 | 1·00832 | −0·00081 |
| 7 | .. .. | 0·126112 | 1·00890 | −0·00023 |
| 8 | .. .. | 0·126112 | (1·00890) | −0·00023 |
| 2 | .. .. | 0·126161 | (1·00929) | +0·00016 |
| 14 | .. .. | 0·126189 | 1·00951 | +0·00038 |
| 11 | .. .. | 0·126198 | 1·00959 | +0·00046 |
| 1 | .. .. | 0·126236 | 1·00989 | +0·00076 |
| 13 | .. .. | 0·126323 | 1·01059 | +0·00146 |
| 5 | .. .. | 0·126422 | 1·01138 | +0·00225 |
| Mean of the unbracketed Nos. (10 experiments) | | | 1·009133 | |

$$r \pm 0·00088,\ r_0 = \pm 0·00029.$$

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* *Proceedings of the Philosophical Society of Glasgow.*

The bracketed values, $x$, are excluded on account of the irregularities in the respective experiments, referred to in the context. For the remaining ten, the mean, the probable error, "$r$," of a single experiment, and the probable error, "$r_0$," of the mean, are given at the foot of the Table. In accordance with the laws of probability, five of the residuals are less, and five are greater, than 0·00088. For a guess at the probable uncertainty of the mean result, let us take the mean of (1) the five lowest and (2) the five highest values of $x$, and divide the difference of the two means by 2. The former mean is 1·00807, the latter is 1·01019; half the difference of the two is 0·00106, or 3·6 times the probable error of the mean, which again falls in fairly well with the law of frequency of error.

Perhaps we had no right to exclude experiment No. 6. If we allow it to vote, the residuals and probable errors stand thus:—

| No. | Residual = $x$ − 1·00868. | |
|---|---|---|
| 6 .. .. | −0·00451 | Mean = 1·00868 |
| 10 .. .. | −0·00138 | |
| 9 .. .. | −0·00051 | |
| 12 .. .. | −0·00100 | $r$ = ± 0·00131 |
| 3 .. .. | −0·00036 | $r_0$ = ± 0·00039 |
| 7 .. .. | +0·00022 | |
| 2 .. .. | +0·00083 | |
| 14 .. .. | +0·00091 | |
| 11 .. .. | +0·00121 | |
| 1 .. .. | +0·00191 | |
| 13 .. .. | +0·00270 | |

Were we asked to name those of our experiments in which we have most confidence ourselves, we should select Nos. 7, 9, 10, 11, 12, 13, 14, because these proceeded with the highest degree of regularity. The mean of these seven experiments, the residuals, and the values, $r$, are as given in the following Table:—

| No. | Residual = $x$ − 1·00882. | |
|---|---|---|
| 10 .. .. | −0·00152 | |
| 12 .. .. | −0·00114 | |
| 9 .. .. | −0·00065 | Mean = 1·00882 |
| 7 .. .. | +0·00008 | |
| 14 .. .. | +0·00069 | $r$ = ± 0·00079 |
| 11 .. .. | +0·00077 | |
| 13 .. .. | +0·00177 | $r_0$ = ± 0·00c30 |

Which of the three means shall we adopt? If there were any considerable difference between them, we should probably say "the mean of the eleven." But the deviations of the three results from one another are only slight, and for this reason we consider ourselves justified in adopting the mean of what we deem to be the seven best experiments as being in all probability the closest approximation to the truth. But, in any case, one correction still remains to be made; we refer to the occluded hydrogen in the metallic copper produced. In the course of our first series, we occasionally determined the occluded hydrogen quantitatively, and arrived at the conclusion that it might safely be neglected. This is still our opinion as far as that series is concerned, but the present, second, series affords a sufficient degree of constancy in the results to justify its application. Unfortunately, however, we arrived at this opinion only after all the work had been completed. The only thing we can do in the circumstances is to try and correct our present results by the occluded hydrogen determinations made in connection with the first series.

As a basis for our calculation, we will adopt four of the determinations quoted on page 105. For these, the uncorrected oxygen weights in grms., and the weights of water obtained from the occluded hydrogen in m.grms., were as follows:—

| Page of Journal. | S. | Water from occluded hydrogen. |
|---|---|---|
| 75 | 10·37 | 3·7 |
| 77 | 10·53 | 2·7 |
| 79 | 10·42 | 2·1 |
| 89 | 15·46 | 7·2 |
| | 46·78 grms. | 15·7 m.grms. |

Take $\epsilon$ as a symbol for the weight of occluded hydrogen per unit-weight of oxygen found, and adopting O = 16 as the standard for atomic weights, the correction to be applied to the uncorrected value of H is $-9\,\epsilon$. The value of $9\,\epsilon$, as calculated from the above numbers, is = 0·0003356, hence we have for the corrected mean of—

| | The 10 unbracketed experiments. | The same and No. 6. | The seven best experiments. |
|---|---|---|---|
| H = .. .. | 1·00879 | 1·00834 | 1·00848 |

The fifth decimal, of course, if of no value whatever; we therefore adopt—

H = 1·0085 (O = 16), or O = 15·866, or say 15·87 (H = 1)

as the net result of our work.

The liquid water produced in the first, and also that produced in the second, series had been carefully collected and preserved in glass-stoppered bottles, and at the end of all the work we examined both for all the impurities that could reasonably be presumed to be present; but we obtained negative results in all cases. Very delicate litmus-paper remained unchanged, no sulphurous acid could be detected by permanganate, no nitrous acid by Griess's reagent, no ammonia by Nessler's, no metals by sulphuretted hydrogen. To test for nitric acid, 10 c.c. of each water were alkalised by addition of a granule of carbonate of soda, and the solution was evaporated to about 0·5 c.c.; oil of vitriol was now added and ferrous sulphate poured on the top of the mixture as soon as it had cooled down sufficiently. There was no colouration even after long standing. To test for sulphuric acid, 5 c.c. of each of the waters was mixed with a drop of chloride of barium, and allowed to stand over night. No trace of a precipitate could be seen, even in the case of the water from the first series, which rather surprised us. We therefore tried to determine the least quantity of $SO_3$, which the test would have revealed. A standard sulphuric acid, containing 40 grms. of $SO_3$ per litre, was diluted with water to 10,000 times its volume, and 5 c.c. of the dilute liquid, containing 0·02 m.grm. of $SO_3$, tested with chloride of barium. After ten minutes a distinct opalescence was seen, but this did not increase on standing, and we felt convinced that an appreciably less quantity could not have been detected. To this extent, therefore, our water from the first series may be contaminated with sulphuric acid.

Being well aware that ours is not by any means the first attempt since the days of Erdmann and Marchand, to fix, as far as possible, the ratio H : O, we will now proceed to a brief review of the results of our predecessors.

Stas (Aronstein's translation of his memoir, pp. 57 and 58).—As the mean of nine experiments which agree almost absolutely with one another, Stas finds that 1 grm. of silver precipitates 0·49597 grm. of sal-ammoniac. Hence taking Ag = 107·93, Cl = 35·454, and N = 14·046, we have $NH_4Cl$ = 53·530, whence $NH_4$ = 18·076, and H = 1·0075, which number, considering that it is burdened with the errors of four experimentally determined constants, agrees wonderfully well with our own. But after all, even Stas's atomic weights cannot be presumed to be free of error, and we need only assume that while his $NH_4Cl$ is by 0·01 too high, his Cl and N are each by 0·01 too low, to bring his value for 4 × H down to 4 exactly. So the agreement, perhaps, is only accidental.

Cooke and Richards (*American Chemical Journal*, vol. x., pp. 81—110, 191—196).—Abstract *Chemical*

*Society's Journal*, "Abstracts," year 1888, p. 647; and *Ibid.*, 910. C. and R. weighed their hydrogen directly in the Regnault fashion; but it is questionable if they gained much by doing so. Even if the hydrogen is absolutely pure, it is questionable whether the weighing of it, as a voluminous gas, affords a higher degree of exactitude than the indirect mode of taking the difference between the weight of the water and the weight of the oxygen, and, if it is contaminated with nitrogen, the indirect method is positively the more exact of the two. C. and R.'s hydrogen, it appears, was dried with oil of vitriol and phosphoric anhydride used together; hence their gas was probably contaminated with sulphurous acid. In their original determinations, they also neglected to allow for the expansion which their hydrogen-globe suffered, when, after having been tared (against a tare-flask of constant displacement) in an exhausted condition, it was filled with hydrogen of the pressure of the atmosphere. After this oversight had been pointed out to them by Lord Rayleigh, they corrected their original results, and found, finally, H = 1·00825, which, as we see, comes close to our own number.

W. A. Noyes (*American Chemical Journal*, vol. xi., pp. 155—161; abstract in the *Berichte der Deutschen Chemischen Ges.; Referate*, year 1889, p. 475).—An apparatus constructed entirely of glass in such a manner that the oxide of copper can be reduced, and the water weighed, within it, is (1) evacuated and weighed. It is then made to communicate with a source of pure hydrogen, the oxide of copper heated, and the water made to condense in the part provided for the purpose, care being taken to keep the oxide of copper slightly in excess. The apparatus is then closed, and weighed. (2) The water is removed by heating the apparatus and sucking out the vapour of water by means of a mercurial air pump. This being accomplished, the apparatus is weighed a third time. Taking $W'$, $W''$, and $W'''$ as representing the three weights, we have, for the hydrogen used, $W'' - W'$; and for the water formed $W'' - W'''$. Six determinations gave (for H = 1), O = 15·905 to 15·876; mean = 15·886 ±0·0028. Or, for O = 16, H = 1·00717.

Lord Rayleigh (*Proceedings Royal Society*, vol. xlv., p. 425).—Two glass globes, of about 1800 c.c. capacity each, are charged, one with hydrogen, and the other with oxygen, of about one atmosphere's pressure, and they are then tared, each against a tare globe of exactly the same displacement. Suitable quantities of the two gases are then extracted by means of a mercurial air-pump (about 0·1 grm. of hydrogen and a slight excess of oxygen), and mixed together in a mercurial gas holder. The large volume of fulminating gas thus produced is exploded, in instalments, in the same eudiometer, and, in the ultimate residue obtained, the oxygen is determined volumetrically, to be reduced to weight by calculation. The weights of oxygen and hydrogen extracted from the globes are determined by weighing the globes after extraction of the gases, the shrinkage owing to the diminution suffered by the internal pressure being allowed for. In this manner all the data for calculating the ratio O : H are procured. Five experiments gave for its value 15·92 to 15·98, without allowing for shrinkage. The correction for it lowers the mean (15·95) by four parts in a thousand, and brings it down to 15·89, corresponding to H = 1·00692, for O = 16. In connection with research by Rayleigh, it is important to notice that he used no oil of vitriol, but only fused caustic potash combinedly with phosphoric anhydride for drying his hydrogen, and took all imaginable precautions for avoiding contamination of his gas with atmospheric air.

Last, not least, we come to that admirable research which E. H. Keiser published in the *American Chemical Journal*, vol. x., pp. 249—261.* Of all the methods used so far for the determination of the gravimetric composition of water, Keiser's impresses me as being the one which offers the surest guarantee for a correct result. Keiser's great hit is that he converts his hydrogen into hydride of palladium and weighs it in this compact form. The condensed hydrogen is re-expelled by heat, burned with oxide of copper, and the water collected and weighed, the displaced air being, of course, allowed for. The palladium (which, in Keiser's case, amounted to about 150 grms.) is contained in a glass tube provided with a soldered-on glass stopcock, constructed like the one characteristic of Lunge's nitrometer, so that we can either send off the liberated hydrogen by the horizontal boring or shut off the palladium-tube, and sweep the rest of the apparatus with a current of nitrogen or oxygen. The first step is to heat the palladium *in vacuo* to 250° for about 15 minntes. The palladium-tube is then made to communicate with an apparatus discharging hydrogen purified; finally, by means of a column of red-hot metallic copper, followed by an U-tube charged with phosphoric anhydride. The hydrogen proper combines with the palladium, the traces of nitrogen with which the gas was contaminated remain outside the palladium, and are removed by means of the air-pump. The exhausted tube is weighed against a tare-tube of the same displacement. It is then connected with the oxide of copper tube, the latter heated to redness, and the apparatus next filled with nitrogen to preclude the possibility of an explosion. After this preliminary operation the hydrogen is being gradually liberated, and converted into water. When the hydrogen is expelled as far as necessary, the palladium-tube is again shut off, and the hydrogen, which stagnates in the rest of the apparatus, swept out by means of a current of nitrogen. At the end the oxygen is turned on and kept going until the reduced copper is completely re-oxidised and its occluded hydrogen recovered as water. Ten experiments gave for the ratio O : H values varying from 15·943 to 15·958; mean = 15·9492, or, for O = 16, H = 1·00318, which is by 0·00529 less than our own adopted value! I have tried hard to explain this not inconsiderable difference, and at last come to conceive the following hypothesis, which I give for what it may be worth. Keiser informs us that he *purified* his nitrogen by passing it successively over oil of vitriol, red-hot metallic copper, and phosphoric anhydride; but he does not tell us how he prepared it. There can, however, be little doubt that he prepared it as other people would have done, namely, by passing a current of purified air over red-hot copper previously reduced in hydrogen. That a man like Keiser should have forgotten to clear out all the *free* hydrogen left in his copper tube before using it for de-oxygenating his air, is not to be presumed, but in whatever way he may have done this, the reduced metallic copper was bound to contain occluded hydrogen, and it is not absurd to presume that this occluded hydrogen *did not all assume the form of water* when the air passed over it at a red heat. His nitrogen, as it came out of the gasholder, may have been contaminated with a trace of hydrogen, and, as a necessary consequence, his number for the weight of water corresponding to two parts of hydrogen may be too high. Supposing, for a moment, that Dittmar and Henderson's value for O : H is the true value, then the 58·86263 grms. of water which Keiser produced in his ten syntheses (out of 6·5588 grms. of palladium hydrogen), included 0·2742 grm. of water from out of the hydrogen of his nitrogen gas; or, in other words, Keiser produced 27·4 m.grms. of adventitious water per synthesis, because the nitrogen gas he used contained, say, 3 m.grms. = about 0·03 litre of hydrogen.

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[*] At the time when we started our investigation, Keiser's experiments were known to me only by his preliminary notice in the *Ber. der Deutschen Chem. Ges.*, in which he gives three determinations of the ratio O : H, the mean of which is 15·872. My impression at the time was, that in all probability, Keiser's palladium hydride contained water, which, by being weighed as hydrogen, made his value for O : H too low. His full memoir I saw for the first time when engaged in the compilation of this paper. If it had come to me in time, the present research would perhaps never have lost its original, purely critical character.—W. D.

I find it difficult myself to believe that it contained so much. Besides, my hypothesis cuts two ways. If nitrogen produced from reduced copper and air is liable to be contaminated with hydrogen, then our own determinations of the occluded hydrogen in certain of the lots of reduced copper which we produced in our first series falls short of the truth; and if they do, our "$H=1·0085$" is liable to a negative correction. Being an incorrigible "Proutian," I do not give up the hope that the true number may be 1·0000 after all.

To sum up, the weight of hydrogen which unites with 8 grms. of oxygen into water is, according to—

| | |
|---|---|
| Dumas's experiments, as corrected by us— | |
| (*a*) Assuming his water-weights are the true weights .. .. .. .. .. | 0·989 |
| (*b*) Assuming that he forgot to reduce his water-weights to the vacuum .. | 1·0002 |
| Erdmann and Marchand's, as corrected by us .. .. .. .. .. .. .. .. | 1·006 |

(These three numbers, of course, are mere guesses, and must be taken for what they are worth).

| | |
|---|---|
| Stas .. .. .. .. .. .. .. .. .. .. | 1·0075 |
| Cooke and Richards .. .. .. .. .. .. | 1·0083 |
| W. A. Noyes .. .. .. .. .. .. .. .. | 1·0072 |
| Lord Rayleigh.. .. .. .. .. .. .. .. | 1·0069 |
| Dittmar and Henderson, the seven best experiments .. .. .. .. .. .. | 1·0085 |

These five independent investigations might be said to settle the question as far as it is possible in the present state of quantitative chemistry to settle it at all, if it were not for—

E. H. Keiser, who finds . .. .. .. .. .. 1·0032

and it is impossible to pass over *his* research!

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*Ordinary Meeting, March 24th,* 1893.

Prof. A. W. Rücker, F.R.S., President, in the Chair.

Several excellent photographs of flying bullets and of the air waves produced by vibrating hammers were exhibited, the originals of which had been taken by Prof. Mach.

A paper on "*The Differential Equation of Electric Flow*" was read by Mr. T. H. Blakesley, M.A.

The object of the paper is to show that the ordinary mathematical expressions for electric flow fail to explain all known facts, and to point out that in order to interpret these facts certain properties of matter not usually recognised must be admitted. The subject is treated both algebraically and geometrically; in the latter case the magnitudes being represented by the projections of the sides of a triangle revolving in its own plane on a fixed line in that plane. Taking the ordinary differential equation for a simple circuit having resistance and self-induction, viz.:—

$$V-L\frac{dC}{dt}=RC,$$

it is shown that this takes no account of any energy except that spent in heating the conductor, and that where radiation into space is concerned, it is necessary to introduce another term, $\lambda C$, where $\lambda$ is a quantity of the nature of resistance. It is further pointed out that if work be done outside the circuit, the line which geometrically represents the induced E.M.F. cannot be perpendicular to that indicating the current and "effective" E.M.F., the latter term being defined to mean the value of the quantity which is numerically equal to the product of the current into the resistance. A magnetic phase-lag must therefore exist. The author also shows that a magnetic field induced in phase with the magnetic induction would not result in a loss of energy, and no hysteresis could exist. Under the same circumstances there could be no radiation of energy from an alternating magnet.

A Leyden jar discharging through a circuit having self induction is next considered. Taking the ordinary premisses, it is shown that no provision is there made for energy radiated into space, and that magnetic lag is necessary for the existence of such phenomena. The differential equations for the variables in condenser discharges, according to ordinary assumptions, are shown to be of the same form, and the variables can be represented by the projection of the sides of a triangle, which is simultaneously undergoing uniform rotation and linear logarithmic shrinking. The rate of shrinking is the same as that of the radius vector of an equiangular spiral of characteristic angle $\beta$, where—

$$\cos\beta=\sqrt{\frac{K}{L}}+\frac{R}{2};$$

K, L, and R representing capacity, self-induction, and resistance, respectively. The equations and their consequences are considered at some length, and several important properties brought out.

To allow for radiated energy, R must be virtually increased from R to $R+\lambda$, and the total energy is divided between the circuit and the field in the ratio of R to $\lambda$. If, therefore, the circumstances be such that $\lambda$ is large compared with R, say by having high frequency, the heating of the circuit may only be a small part of the total energy. In this direction the author thinks the true explanation of some of Tesla's experiments is to be found, the energy being expended chiefly in radiation and not in current through the experimenter's body. When obtaining photographs of rapidly moving objects, Prof. Boys had used discharges of high frequency, but since several sparks of nearly equal intensity were obtained, the decay of amplitude was not very rapid, and the angle $\beta$ of the logarithmic spiral representing the magnitudes would be nearly 90°. For the most rapid discharge $\beta=45°$, and the ratio of successive maxima was $\epsilon^{\pi}:1$, *i.e.*, 23·14 to 1.

Prof. Perry thought the $C^2R$ term would not represent the heating of the wire when the oscillations were rapid, owing to the distribution of current not being uniform over the section of the conductor. Maxwell had shown that certain throttling terms had to be considered. In condenser discharges the complete equation would have many terms.

Prof. O. J. Lodge said the best definition of R in such cases was that derived from Joule's law rather than that of Ohm. Frequency was very important in the radiation of energy, but even at ordinary frequencies of alternators some energy was radiated. Referring to Tesla's experiments, he said the reason why no serious consequences followed was that there was not much energy behind them. High frequency might be instrumental in preventing injury, but this he thought remained to be proved.

Dr. Sumpner pointed out that losses other than $C^2R$ (R being the ordinary resistance of the conductor) had to be taken into account. In some cases, such as transformers on open circuit, the effective resistance might be one thousand times that of the coil. To discuss completely the problem taken up by Mr. Blakesley, it would be necessary to take account of non-uniform distribution of current both across and along the conductor, as well as the character of the magnetic and electric fields surrounding the circuit.

Mr. Swinburne thought there was a tendency to over estimate the rate of high-frequency currents, for unless the coils of transformers were assumed geometrically coincident, calculations were difficult. Errors of hundreds per cent were quite possible. In Tesla's experiments no great power was involved, for the transformer could not give out any large power.

Mr. Blakesley, in reply, said the term R was such that $C^2R$ represented the whole waste in the conductor, whilst $\lambda$ included everything wasted outside the conductor.

A paper on "*The Viscosity of Liquids*," by Prof. J. Perry, F.R.S., assisted by J. Graham, B.A., and C. W. Heath, was read by Prof. Perry.

The viscosity was tested by suspending a hollow cylinder within an annular trough containing the liquid and measuring the torque exerted on the cylinder when the trough rotated at various speeds about its axis. In the paper the equation of motion under the conditions of the experiment is discussed, the error introduced by assuming that the liquid moves in plane layers being shown to be about 0·5 per cent. To determine the torsional constant of the suspending wire, two methods were employed; in one, the turning moment required to produce a given angular movement was measured directly, and in the other, the torsional constant was determined from the period of oscillation. By measuring the viscous torques exerted with different depths of liquid in the trough, the correction for the edge of the suspended cylinder was found to be 0·8 c.m. On plotting the results obtained with sperm-oil at different temperatures and constant speed, a discontinuity was noticed about 40°. For a speed of 9 revs. a minute, the viscosity ($\mu$) could be very approximately calculated from the formula $\mu = 2{\cdot}06(\theta - 4{\cdot}2)^{-0{\cdot}686}$ below 40° C., and—

$$\mu = 21{\cdot}67(\theta - 4{\cdot}2)^{-1{\cdot}349}$$

above 40° C., $\theta$ being the temperature. Experiments on the change of density of sperm-oil with temperature, made by Mr. J. B. Knight, indicated a minimum density about 40°. Subsequent experiments with other samples had not confirmed these observations. The paper contains several tables of the results obtained in various experiments. Those performed at constant temperatures show that for slow speeds the torque is strictly proportional to speed, but afterwards increases more rapidly, probably owing to the critical speed having been exceeded. The authors had also attempted to determine the viscosity from the damping of the torsional vibrations of the suspended cylinder, but the mathematical difficulties were found to be considerable.

After concluding the paper, Prof. Perry read a letter he had received from Prof. Osborne Reynolds on the subject, who doubted whether the true critical velocities had been reached in the experiments. In the particular arrangement employed, he would expect no critical velocity in the outer ring of liquid, whilst in the inner ring the motion would be unstable from the first.

Prof. Lodge said he had tried whether the refraction or the density of sperm oil exhibited a discontinuity about 40°, but found none.

Mr. Rogers pointed out that experiments which corroborated those of Prof. Perry had been made by M. Couette, and published in *Ann. de Chim. et de Phys.* [6], xxi.

Mr. E. W. Smith suggested that the apparent discontinuity might be due to the separation of the constituents of an impure oil at certain temperatures and speeds of revolution.

**Preservation of Constant Temperatures above the Boiling-Point of Water.**—K. Ulsch (*Zeit. f. Brauwesen*).—The author connects a closed water-bath, by means of a flexible tube, with the upper end of a glass cylinder containing water and below it mercury. The pressure on the surface of the water forces the mercury into an ascending tube expanded above to a ball. Into the tube there opens a glass tube, cut off obliquely below, and leading to a burner below the water-bath. Gas is supplied by a tube opening laterally into the ball. The apparatus acts like an ordinary thermo-regulator.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

### *Bulletin de la Société Chimique de Paris.*
### Series 3, Vols. ix. and x., No. 2.

**Polimarimetic Examination of Gums.** — M. Guichard.—On examining the rotatory powers of gums they are found to form three series: those of Galam, Mogador, and Australia have a rotatory power near 16. Gums Arabic, Aden, and Amrad border upon 32, whilst gum Gatti has a rotatory power close upon 64. The facts may be explained by the view that the gums are mixtures of several dextro-rotatory and lævo-rotatory substances.

**On the Spontaneous Inversion of Cane-Sugar in an Aqueous Solution, and on the Cause of this Inversion, apparently Spontaneous, under the Influence of Light.**—A. Béchamp.—The hypothesis of the inversion of cane-sugar by water alone in the cold must be rejected, and when it is apparently produced spontaneously the cause must be sought in the microzyme or a mould.

**Action of Phenylhydrazine upon Camphoric Anhydride and the Camphoric Ethers.**—C. Friedel and A. Combes.—The formula proposed by one of the authors to represent camphoric acid leads us to admit a ketonic function in the molecule of this acid, and of its anhydride. In the present paper they seek to demonstrate the existence of this function.

**Sulpho-conjugated Compounds of Camphor and their Derivatives, Propylnitrophenol and Propylamidophenol.**—P. Cazeneuve.—The acetylic derivatives with which the author chiefly concerns himself absolutely confirm the nature of the propylamidophenol, whilst its other properties and its mode of production confirm the constitution assigned to it by the author.

**Constitution of Camphor.** — P. Cazeneuve. — In consequence of facts recently discovered, we are more than ever authorised in declaring that an array of imposing facts gives a powerful support to the theoretic conception of Kekulé, which must remain founded in its essential features.

**Facts Serving for the History of Gum Arabic.**—A. Béchamp.—The author's experiments necessitate the conclusion that gum arabic contains a zymase which transforms amylaceous matter.

**General Theory of Chemical Action.**—E. Maumené.—The author claims the priority as against M. Raoul Pictet of the ascription to gravitation of a great part in chemical phenomena.

### No. 3.

**On Calcium Tartrate Extracted from the Dregs of Distilleries, its Determination and its Refining.**—Ch. Ordonneau.—Already inserted.

**The Rotatory Power of Grape-Must in Algeria.**—H. and A. Malbot.—The rotatory power is very variable according to the ripeness of the grapes, the topographic position of the soil, and the nature of the cultivation. The alcoholic standard increases much more rapidly as the lævorotatory power decreases. It seems to the author that between saccharose and invert sugar there exists normally in grapes, at least in warm climates, a lævorotatory compound which differs from saccharose by its greater resistance to inversion.

**New Method for the Determination of Fluorine.**—A. Carnot.—This paper requires the three accompanying figures.

**The Formula of Ordinary Tartaric Acid.**—Albert Colson.—(A reply to MM. Friedel and Le Bel).—The author shows that the stereochemical theories are neither simple nor clear, and that the notion of the product of dissymmetry based upon these theories is found once more in fault. It sins either in itself or in its foundations.

**Action of Alkaline Alcoholates upon Camphoric Anhydride and other Anhydrides; Formation of Camphoric Ortho-Ethers.**—P. Cazeneuve.—As the allo-ethers are still less easily saponifiable (Friedel) than the ortho-ethers, it appears that the analogies of camphoric acid with the succinic and phthalic acids are so remote that, like Friedel, we may search for novel interpretations.

**On New Explosives.**—A. Berg and L. C. Mautrand.—The hypophosphites mixed with chlorates form interesting explosives which seem to admit of applications. One mixture mentioned consists of equal parts of barium hypophosphite and potassium chlorate dried and powdered separately. If ignited in a confined place it has a shattering effect like that of mercury fulminate. It may be detonated by a slight shock or by the electric spark. Mixed with an equal quantity of magnesium powder it may be used for photographic purposes. Another mixture is that of sodium thiosulphate in a syrupy solution and powdered sodium chlorate. A drop heated on thin tinsel liquefies, boils up, dries, and gives an explosion like that of nitroglycerin.

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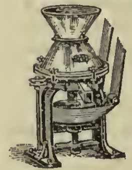
*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. vii., No. 84.

**Animal Charcoal.**—Fiquier, a pharmacist of Montpellier, discovered the absorbent properties of animal charcoal in 1811. Devosne used it in 1812 to purify the juice of beets. Its regeneration was first attempted by Dumont in 1828. In Austria the manufacturers of sugar use their bone-black in large fragments up to the size of a walnut and wish for a porous product. In Germany the grains of the black must not exceed the size of a filbert, and must be as hard and compact as possible. The proportion of carbon must be 8 per cent, and the moisture must not exceed 8 per cent. In France the animal charcoal is required in grains varying from the size of linseed up to that of a filbert. Certain consumers demand at least 10 per cent of carbon and at most 6 per cent of moisture. In England and America the product is consumed almost exclusively of the size of millet-seed, as hard and as spherical as possible. The bones before carbonising are treated with light hydrocarbons of petroleum to remove the grease. The residue is dried at 70°, broken up into fragments, and charred in retort furnaces. The volatile oil given off (Dippel's oil) serves for denaturising alcohol. The thickness of the mass in the retorts should not exceed 20 c.m. The decolourising action of animal charcoal is explained by F. Schiller on purely physical principles, whilst Birnbaum and Bomasch recognise a chemical action.

## MEETINGS FOR THE WEEK.

MONDAY, 10th.—Medical, 8.30.
TUESDAY, 11th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "Symbolism in Ceremonies, Customs, and Art," by John Macdonell, LL.D.
WEDNESDAY, 12th.—Geological, 8.
—— Pharmaceutical, 8.
THURSDAY, 13th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
FRIDAY, 14th.—Royal Institution, 9. "Seals," by Sir William H. Flower, F.R.S.
—— Astronomical, 8.
SATURDAY, 15th.—Royal Institution, 3. "Some Applications of Electricity to Chemistry," by James Swinburne, M.Inst.E.E. (The Tyndall Lectures).



THE CHEMICAL NEWS.

Vol. LXVII., No. 1742.

## RESEARCHES ON THALLIUM.
## RE-DETERMINATION OF ITS ATOMIC WEIGHT.

By M. CHARLES LEPIERRE.

I have been led, in consequence of previous researches undertaken in concert with M. Lachaud (*Comptes Rendus*, 1891, July 27th), to undertake a re-determination of the atomic weight of thallium. The data furnished by different chemists vary in fact from 203·5 to 204·8, and the determinations have always been effected on thallous salts. In these experiments I have used the pure crystalline thallic oxide, $Tl_2O_3$, described by me (*loc. cit.*), as also thallous compounds, to admit of a comparison of the methods. Commercial thallium in large quantities was submitted to a complete purification. We employed the electrolytic method, both alone and associated with M. Bautigny's process. The process followed for obtaining thallic oxide was as follows.

In our first experiments we obtained $Tl_2O_3$ by fusing thallous chromate with potassa. This process is not beyond criticism as regards the possible presence of chrome (though we have not detected it in our samples). I now employ simply the sulphate or nitrate, less commonly thallous chloride, melting them below a dark red heat with eight or ten times their weight of *pure* potassa. The hexagonal tablets of $Tl_2O_3$ formed are easily separated from the excess of potassium hydroxide or sulphate by washing with water until all alkalinity has disappeared and the potassium rays are no longer visible with the spectroscope. The oxide thus prepared dries easily and does not lose oxygen below light redness. It is easily converted into thallous sulphate by means of sulphurous acid.

I have employed four different methods for the determination of the atomic weight:—

A. Weight of thallium obtained by the electrolysis of thallous sulphate.

B. Weight of thallium contained in $Tl_2O_3$ after conversion into $Tl_2SO_4$ and electrolysis.

C. Weight of thallic oxide formed by the fusion of thallous salts with potassa.

D. Proportion between thallium and oxygen on the reduction of $Tl_2O_3$ or hydrogen.

The first method gave for the atomic weight of thallium numbers varying from 203·52 to 203·69; the second yielded numbers comprised between 203·53 and 203·73; the third numbers from 203·44 and 203·79; and the fourth values comprised between 203·54 and 203·60.

The mean of these eleven determinations, selected from those which seem to have been most successfully executed, leads to the figure 203·62, a little below the value 203·7 which has of late been generally admitted without proof. Recent determinations of atomic weights generally tend to reduce the values adopted.—*Comptes Rendus*, cxvi., p. 580.

[M. Lepierre has thought it advisable to re determine the atomic weight of thallium. In so doing he remarks that "the value 203·7 has of late been generally admitted without proof." It may, in return, be fairly asked what guarantee does he furnish for the accuracy of his own results? If we compare his memoir with that of Mr. Crookes (*Philosophical Transactions of the Royal Society*, read June 20, 1872), we are at once struck with the fact that M. Lepierre omits, or at least makes no mention of, those elaborate and minute precautions which Mr. Crookes found necessary in order to eliminate the possibility of error. M. Lepierre makes no mention of the balances employed, of any corrections for pressure and temperature, of any adjustment of weights, of precautions taken to ensure the purity of the chemicals employed, and especially of the thallium itself. He admits, indeed, the "possible presence of chrome" in one of his processes, though he was not able to detect it.

We cannot help noticing how completely, in a research of this kind, M. Lepierre omits all criticism of, or even mention of, the work of Mr. Crookes. It is a practice too common among our neighbours on the other side of the channel to ignore all work not published in the *Comptes Rendus* of the Academy of Sciences. It would have been more satisfactory, and we venture to say more truly scientific, had M. Lepierre criticised the work of Mr. Crookes, pointing out any additional precaution which might or could have been taken, and any error either in principle or in detail. In a matter of such fundamental importance as the determination of an atomic weight, this demand cannot be pronounced superfluous or excessive.

We, in turn, cannot well criticise M. Lepierre's results without a more thorough account of his procedures than he has seen fit to furnish.]

## ON THE PURIFICATION OF WATER USED FOR STEAM-BOILERS.*

By R. JONES, Ph.D.

Although the injurious effects of boiler deposits is a common experience with all users of steam power, surprisingly little seems to be done in the way of combating the evil. From a paper by Betke, of Stettin, read at the last annual meeting of the (German) Society for Boiler Inspection, it appears that out of a total of 27,600 boilers inspected only 5480, or less than a fifth, were provided with any means at all of protection against incrustation, which is, I think, a sufficient proof that the importance of the subject has not as yet very deeply impressed those immediately concerned. And this, be it said, notwithstanding that the subject is one offering every possible inducement to its study.

A boiler, for example, fed with hard water, has to be laid off for cleaning oftener than one supplied with softened water, and the loss this entails, added to the cost of cleaning, may amount in the course of a year to almost the cost of a permanent plant for the purification of the water.

Then, again, boiler incrustation, on account of its bad conductivity, causes a greater consumption of coal. In a case referred to by Münter, the work of ten boilers was, after the erection of a suitable water softening plant, compassed by seven. Owing, also, to the bad conductivity of the incrustation, the boiler plates become over-heated, sometimes even red hot, and as a consequence are sooner destroyed. Many boiler explosions may, in fact, be traced to this cause, viz., to allowing the accumulation of too great a thickness of deposit. And then, lastly, there is the injury done to the boilers themselves by the operation of chipping off the deposit, which is by no means an inconsiderable item in the account.

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* From the *Zeit. Angew. Chemie*, 1892, p. 15.—Communicated by H. H. B. Shepherd.

Any one of these reasons in favour of water purification, viz., less frequent laying off, saving in cost of cleaning, diminished consumption of coal, longer life of the boilers, and greater security against explosion, might indeed be held sufficient of itself to justify the erection of a water softening plant.

To what, then, can be attributed the prevailing neglect of this subject? Most frequently, I think, it arises from simple indifference, force of habit, and aversion to any kind of innovation; especially when expense is likely to be incurred, though some, no doubt, are deterred by the discouraging experience of their own or of others, due to experimenting with unsuitable plant. Then the number of doctors and empirics always ready to compete for the honour of ministering to the complaint makes the choice between them exceedingly difficult if one has not the opportunity of making the subject a special study, and, moreover, as every year sees new and presumably improved proposals brought forward, it is scarcely surprising that some should decide to wait until an absolutely perfect system shall have been produced.

Leaving, however, the conflict between the good and the better, let us pass on to consider what has already been accomplished, and I think we shall find that technical chemistry is even now able to satisfy the requirements of a good water purifying process.

In connection with water purification we have principally to consider three groups of salts.

1. Calcium and magnesium carbonates.
2. Calcium and magnesium sulphates.
3. Calcium, magnesium, and sodium chlorides.

The insoluble carbonates are held in solution by carbonic acid contained in the water. Simple boiling occasions the expulsion of the carbonic acid gas and the separation and precipitation of the carbonates as sludge, the sulphates and chlorides remaining in solution. In the boiler, however, in which naturally the same takes place as boiling in a beaker, the latter salts become more and more concentrated, since we are continually adding impure water containing these salts in solution and withdrawing pure water in the form of steam, so that in course of time the calcium sulphate which possesses a solubility of only 1 in 500 also begins to separate out. This separation, however, does not take place suddenly, and in the form of sludge, as in the case of the carbonates, but proceeds slowly, forming a crystalline incrustation enclosing the muddy carbonate deposit within itself. This coats the boilers, more especially on the parts in contact with the fire, and becoming baked on, produces the usual boiler incrustation. The magnesium salts and the chlorides remain in solution, the concentration never being carried so far as to cause the separation of these also. In addition, however, to the dissolved salts, many waters contain mechanical impurities such as earthy matter held in suspension, and these, through the constant ebullition, form into balls, which, settling down with the separated salts, become baked on, and so increase the quantity of the incrustation.

It is now apparent to the chemist by what means the purification of the water can be accomplished. The carbonates can be removed either by simple boiling or by withdrawal of the carbonic acid by addition of quicklime or caustic soda. The sulphates may be dealt with either by depriving them of their sulphuric acid by addition of barium chloride, or by precipitation of the lime and magnesia by sodium carbonate and caustic soda. The chlorides and alkaline salts must remain in solution, there being at present no practical means for effecting their removal. Their accumulation in too great quantity can only be guarded against by frequent sludging, and it is desirable for the sake of the boilers that this should be carefully attended to. But the chemical is the smallest, perhaps even the most unimportant, side of the question. The main problem is how the purification can be carried out.

In this connection valuable information is supplied by the statistics of the Society for Boiler Inspection. In Betke's paper, already referred to, we find the following:

In 3800, or 15 per cent, softening of the water is effected inside the boilers themselves by decomposition of the calcium sulphate by sodium carbonate, barium chloride, or some other reagent; in 1400, or 5·5 per cent, the boilers are fed with chemically purified water; in 150 cases, or 0·6 per cent, the water is softened as above in the boilers, and the resulting precipitate caught by a dejector apparatus; and in 130 cases, or 0·5 per cent, the water is simply mechanically purified by filtration through sand or sponge. This last, however, lies outside the scope of our inquiry, as a simple filtration can be of use in only isolated cases, and then it is not merely useful but necessary; in all other cases an improvement of the water by such means is out of the question. As regards the 3800 boilers in which sodium carbonate or barium chloride is added direct, the society reports that this procedure mostly gives satisfaction. Where this process is suitable it is at any rate the cheapest, since no extra plant is required, and the only expense is the trifling cost of the reagents used. If it answers the purpose, it is of course necessary to maintain always a slight excess of soda in the boiler, as otherwise the incrustation, though diminished, will not be entirely prevented. Frequent sludging and regular testing of samples for excess of soda are also necessary to ensure a good result. Phenolphthalein answers well for this purpose, and a solution can be given to the workman in charge of the boilers.

In only the small number of 150 boilers, or 0·6 per cent, is the deposit removed by means of a dejector apparatus placed inside the boiler. Such an apparatus, however, is, as Fischer has shown, powerless to prevent the incrustation caused by the separation of calcium sulphate, and it is therefore necessary, in conjunction with it, to employ means to soften the water. The older apparatus of Popper and Schmitz appear to have been entirely abandoned. According to the statistics of the Boiler Inspection Society, the apparatus of Dervaux is used with 105 boilers, that of Schröder-Guben with 40, and that of Grimm, Natalis, and Co. with 5. The plan is favourably reviewed in the collective reports of the Society.

If, however, expense has to be incurred for fresh plant, it is certainly better to prevent the precipitate passing into the boiler at all than to provide means for its removal when there by a separate apparatus, and that this is the opinion of the majority is shown by the fact that against 150 boilers fitted with dejectors inside, there are 1400 fed with chemically purified water. Dervaux also, who alone has provided 75 per cent of these apparatus, must be of the same opinion, since two years ago he brought out a water purifying apparatus, which if not the best, is at any rate one of the best in existence.

Of the boilers fed with chemically purified water—

640 make use of the old plan of settling-tanks.
280 ,, ,, Dehne's filter press system.
250 ,, ,, Gaiblet's apparatus (Humbold's engineering works).
61 ,, ,, Bohlig and Heyne's plan.
54 ,, ,, the Dervaux plan.
255 ,, ,, the systems of Bérenger Stingl, Reichling, Hohenzollern, Klein, Schanzlin, and Becker, or Reinecke.

To attempt a detailed description of these various and in some respects very ingenious apparatus would go beyond the scope of this paper. In the settling-tank the water to be purified is carefully mixed with the proper chemicals and heat applied, and after the precipitate has settled out the clear water is drawn off. This process is both cheap and simple, and has the only fault of occupying too much space. As a rule one settling tank is not sufficient; indeed, for a large establishment a series would be needed, and then the whole time of one man would be required to take charge of it.

The apparatus of Humbold and of Dervaux are constructed on the principle of the settling tank. The water ascends from the bottom of the tank and impinges upon pillar-shaped plates placed one above the other, on which the sludge deposits. Reichling has a construction of his own with cloth and sand filters, Dehne and Klein, Schanzlin, and Becker filter direct through presses after boiling in small vessels with the chemicals.

The apparatus, *per se*, however, has nothing to do with the chemical purification of the water, and not one of these different systems can accomplish more than the simple settling tank, *i.e.*, produce clear water; they possess the advantages, however, of requiring but little space and of facilitating and simplifying the addition of the chemicals.

The following chemicals have been proposed for precipitating the salts which cause incrustation :—

1. Materials containing tannic acid. These are less effective than soda, and have the disadvantage of causing the water to froth; moreover, as they have not as a rule cheapness in their favour, they are very properly going more and more out of use.

2. Quicklime and barium chloride, first proposed by De Haën. To a given quantity of cold water milk of lime is added by degrees, whilst stirring, until it just commences to show a feeble reaction with turmeric or red litmus paper; solution of barium chloride, calculated according to the analysis of the water, is then added, the whole stirred and heated to boiling. The quicklime precipitates the carbonates of lime and magnesia in the form of a flocky precipitate, which carries down with it the otherwise slow-settling barium sulphate. In half an hour the water settles quite clear and can be drawn off. This process from the point of view of the removal of the salts causing incrustation is excellent. Beyond the chlorides originally contained in the water, nothing is now left but the lime of the gypsum (also in the form of chloride) and of course the excess of the reagents used. Herein, however, lies the weak point of the process. A small excess of barium chloride matters but little, but an excess of milk of lime produces an incrustation of the worst possible kind. This danger, however, it is said, can be avoided by the use of the lime saturator of Dervaux, in which milk of lime, which necessarily varies in strength, is replaced by saturated lime-water of constant composition. An excess of lime added in the form of lime-water cannot be otherwise than very trifling except through carelessness, and even then is easily removable by a little carbonate of soda. There is another point in connection with De Haën's system which should be mentioned, viz., that the chlorides are liable to accumulate in the boiler water to an injurious extent. This evil, which is more or less common to every water purifying system, must be counteracted by daily sludging, and it is quite possible by this means in most cases to keep the concentration within harmless limits.

3. A third anti-incrustrator which has been recommended is magnesia hydrate (Bohlig and Heyne's patent), of which the inspectors' reports speak very favourably (61 boilers are mentioned as being fed with water purified in this way); the result, however, can only be considered satisfactory if the water be poor in calcium sulphate.

4. The anti-incrustator in most general favour is carbonate of soda, either alone or in combination with quicklime or caustic soda. Even when used alone this reagent accomplishes all that could fairly be expected in the way of water purification. It is simple in application, precipitates the lime and magnesia almost completely, and has the distinct advantage which cannot be too highly esteemed, that the addition of too large an excess is perfectly harmless. When, however, carbonate of soda is used, it is very important that the boilers should be blown off regularly every day, or in time the concentration will reach a point when the solution will have a higher boiling-point than that of water, and be liable to exert a corroding influence upon the plates, packing, &c., of the boilers.

(To be continued).

## ON METALLIC OSMIUM.

By A. JOLY and M. VEZES

Osmium, as generally obtained by the method of Berzelius, *i.e.*, by igniting the sulphide in a crucible of carbon, is a powder or a spongy mass of a more or less deep blue colour, according to its state of division. It is then directly oxidisable in the air, and exhales a very strong odour of osmic acid. H. Sainte-Claire Deville and H. Debray obtained osmium in small crystals of a fine blue tinted with grey by passing fumes of osmic acid into a tube of carbon very strongly heated. The specific gravity of the metal has been successively represented by the numbers 7, 10, and 21·4; the specific gravity of crystallised osmium is 22·48.

H. Sainte-Claire Deville and H. Debray attempted unsuccessfully to fuse osmium by heating it before the oxyhydrogen blowpipe in a crucible of coke enclosed in a crucible of lime. If directly heated in the point of the blowpipe flame, the metal disappears rapidly, either by volatilisation or by conversion into the volatile peroxide. But even an experienced eye which follows the phenomenon attentively cannot detect in the morsels of osmium as they rapidly disappear the least trace of fusion. In order to solve this question osmium must be heated in a vacuum by means of a powerful arc. In consequence of its physical and chemical properties, which, however, vary according to the manner of its preparation, osmium approximates to the non-metals. According to Deville and Debray, it is the non-metal of the platinum family. Berzelius assimilates it to arsenic and Dumas to tellurium.

Perfectly pure osmium may be melted in the electric arc, and obtained in a metallic form comparable to ruthenium. On account of its oxidability, the poisonous character of its vapours, and to avoid losses by volatility, which render the experiments very costly (the lowest price of the metal being 1500 fr. per kilo.), it is necessary to adopt special arrangements. We operate in a closed apparatus traversed by a slow current of carbonic anhydride and in cupels of coke. If the metal is rapidly raised to the highest temperature of the arc, it melts without being appreciably volatilised.

We succeed badly if we operate in lime crucibles; in contact with the metal the lime is profoundly converted into a vitrifiable mass, with which the metal remains incrusted.

Melted osmium is very brilliant on the surface; the colour is still a bluish grey. Further experience must decide whether the metal is blue just as gold is yellow and copper is red. The fracture is crystalline, harder than iridium and ruthenium; it cuts glass deeply, scratches quartz, but is scratched by topaz; the best tempered files do not cut it. If thus melted osmium is not oxidised in the air at common temperatures.

Osmium as a metal may be compared to ruthenium; these two metals form a very distinct group—like rhodium and iridium on the one hand, and palladium and platinum on the other. The atomic volumes are almost identical.

| | Atomic weight. | Specific gravity. | Atomic volume. |
|---|---|---|---|
| Ruthenium .. .. | 101·4 | 12·06 | 8·40 |
| Osmium .. .. .. | 190·3 | 22·48 | 8·46 |

More refractory than all the other metals of the platinum group, they are more readily oxidised, and if heated to redness in oxygen they yield peroxides $RuO_4$ and $OsO_4$.

They approximate greatly to Mn by their very extensive series of oxides of an acid character.

The double chloride $OsCl_4,2KCl$ establishes the connection of the group with the platinum-palladium group, as well as with iridium. Ruthenium has no corresponding compound. Rhodium is similarly situated, and the compound $PtCl_4 2KCl$ is not stable. The tetrachloride and its derivatives, so characteristic of platinum, are merely an exception for the three metals of the group, the atomic weights of which are comprised between 101 and 106. The double sesquichlorides $Ru_2Cl_6 2KCl$ and $Os_2Cl_6,2KCl$ connect them by rhodium and iridium.—*Comptes Rendus*, cxvi., No. 11.

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## SEPARATION OF MERCURY FROM THE METALS OF THE SO-CALLED ARSENIC AND COPPER GROUPS.

### INAUGURAL DISSERTATION, GÖTTINGEN.

By K BÜLOW.

THE author treats the sulphides with a mixture of equal parts of equally concentrated solutions of potassium hydroxide and sulphide. In this mixture arsenic, antimony, tin, and mercury sulphides dissolve, whilst the sulphides of the copper group remain unaffected.

From the solution of the sulphides of mercury and of the arsenic group, the mercury is easily re-precipitated as sulphide on the addition of ammonium chloride. The author used a 15 per cent potassa-lye. It was mixed with a few drops of solution of potassium sulphide, and the clear solution was drawn off with a syphon from the subjacent black precipitate of iron sulphide.

In order to obtain the solution of potassium sulphide a 15 per cent potassa-lye was divided into two parts; one of these was saturated with sulphuretted hydrogen, and the other part was then added. The clear solution was drawn off with a syphon from the precipitate which forms on prolonged standing in heat, and the solution of the potassium sulphide, like that of the potassium hydroxide, is preserved in well-fitting vessels. The solution of ammonium chloride used was purified from a possible proportion of iron by the addition of a few drops of ammonium sulphide, and the precipitate formed was filtered off.

For separating mercury from bismuth, 0·2 grm. mercuric chloride and an equal weight of bismuth oxide was dissolved in concentrated hydrochloric acid, and sulphuretted hydrogen was passed into the solution, which had been carefully diluted with hot water. After the bismuth has been precipitated it is largely diluted with hot water, and sulphuretted hydrogen is again introduced until the liquid is saturated.

After the precipitate has been filtered off and washed, the filter is perforated, and the precipitate is rinsed back into the beaker with hot water, to which a few c.c. of the above mixture of equal parts of potassa-lye and solution of potassium sulphide are added. The precipitate is then digested with from 20 to 25 c.c. of the above mixture; the liquid is then boiled once, diluted with hot water, and the bismuth sulphide remaining undissolved is filtered off. It is washed with water, to which a few drops of the mixture has been added. In order to bring absolutely all the mercury sulphide into solution, 10 c.c. of the mixture must be used to about 0·1 grm. of mercuric chloride taken.

The filtrate which contained the mercury was mixed with solution of ammonium chloride until no further separation of mercury sulphide takes place. The precipitate, which is at first finely pulverulent, readily clots together, and is deposited clear if the liquid is heated for some time on the water-bath.

The mercury sulphide is filtered, washed with water containing ammonium sulphide, and then returned to the beaker together with the filter and covered with cold water. Potassium chlorate is then added, the whole well stirred up and mixed with a sufficiency of concentrated hydrochloric acid. The mercury sulphide dissolves rapidly and completely. The excess of chlorine is expelled on the water-bath, the filter residues are filtered out and washed with hot water containing hydrochloric acid.

The filtrate was largely diluted, heated to about 90°, and saturated with sulphuretted hydrogen. If it is not sufficiently diluted, and if the solution is not heated, the precipitate settles very badly, and the quantity of mercury is found deficient up to 15 per cent. The mercury sulphide was filtered through a filter, dried at 102° and weighed, washed with sulphuretted hydrogen water to which a few drops of concentrated hydrochloric acid have been added, dried at 102°, and weighed.

The determination of the bismuth can be effected according to one of the ordinary methods. This process effects a complete separation of mercury from bismuth. Mercury may be separated from copper, silver, and lead in a quite similar manner.

The method is, however, not applicable to the separation of mercury from cadmium, since a large part of the mercury sulphide remains undissolved along with the cadmium sulphide. Nor can the separation of the two metals be effected by treating the sulphides with nitric acid, since a considerable part of the mercury sulphide remains undissolved along with the cadmium sulphide. The author shows that zinc sulphide cannot be separated from mercury sulphide by digestion with the above mentioned mixture.

For separating mercury from arsenic, 0·2 grm. each of arsenious acid and mercuric chloride were dissolved in concentrated nitric acid, and the excess of the latter was evaporated off as far as possible. After the solution obtained had been largely diluted, it was saturated with sulphuretted hydrogen. The precipitate formed was filtered off after standing for a long time, and digested as above described with the solution already named. The clear solution thus obtained was slightly diluted, boiled up, and mixed with solution of ammonium chloride until no further separation of mercury sulphide occurs. It is then heated on the water-bath and the mercury sulphide is filtered off. The arsenic sulphide in the filtrate is determined by a usual process, whilst the mercury is determined as above described.

In separating mercury from antimony, 0·2 grm. antimony oxide and an equal weight of mercury chloride were dissolved in concentrated hydrochloric acid. It was then oxidised with potassium chlorate, mixed with tartaric acid after the expulsion of the excess of chlorine, diluted, heated, and the solution saturated with sulphuretted hydrogen. The further treatment may be inferred from what has been said on the separation of mercury and arsenic.

Whilst this method gives good results for the separation of mercury from arsenic and antimony, it is not applicable to the separation of mercury from tin. Ammonium chloride throws down from the solution of the sulphides a part of the tin, along with the mercury sulphide, and some mercury remains in solution along with the main quantity of the tin.

Of course, mercury can be separated by the above method if several of the above metals are present simultaneously, cadmium and tin being excepted.—*Zeit. Anal. Chemie*, vol. xxxi., p. 697.

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**Examination and Correction of the Saccharometer Scale.**—K. Ulsch (*Zeit. fur Brauwesen*) suspends the instrument from the hydrostatic balance, and for the several degrees of the scale determines the loss of weight which the instrument undergoes when plunged into pure water at 14° R. To find the true value of this degree of the scale, the weight of the saccharometer is divided by the loss of weight.

# THE ANALYSIS OF IRON AND STEEL.[*]

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

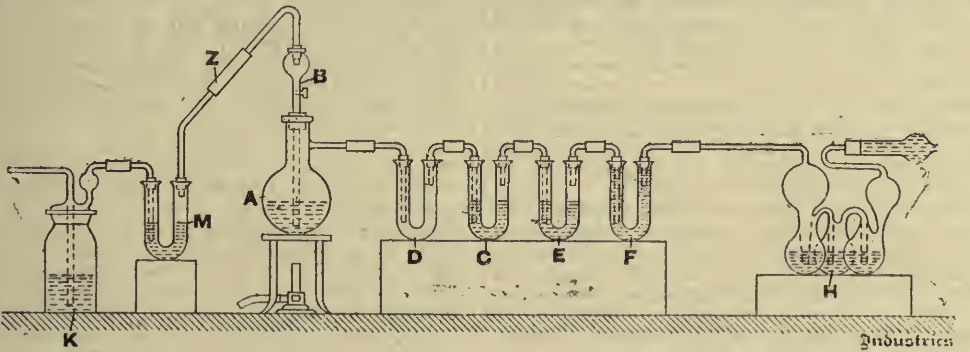
(Continued from p. 162.)

*Total Carbon.*—There are at least two conditions in which carbon may exist in iron and steel, viz., (1) in chemical combination with the iron, and (2) in the free state as graphite or graphitic carbon. In steel it is considered that there is a third form of carbon termed "cement carbon," which has considerable influence upon the quality of the metal under varying conditions of temperature, &c. As is well known, upon dissolving iron or steel in hydrochloric acid, the iron enters into solution as ferrous chloride with the evolution of hydrogen, which, being in the nascent condition, combines with any combined carbon present, forming volatile hydrocarbons, while the graphitic carbon remains intact. If, however, the iron be dissolved in such a manner as to prevent the evolution of hydrogen, no hydrocarbons are formed, and the combined, together with the graphitic carbon, is deposited in an insoluble form, which may be collected and burnt, and the resulting carbonic acid ($CO_2$) weighed directly or indirectly. Such is the action when the metal is treated with a solution of ammonium cupric chloride or copper sulphate; the iron displaces the copper and enters into solution, while the combined and graphitic carbon, together with copper, are deposited.

The determination of the total amount of carbon consists of two operations—(1) the preparation of the carbonaceous residue for subsequent treatment, and (2) the determination of the carbon contained in this crude residue.

*Preparation of the Carbonaceous Residue.*—Dissolve 280 grms. of ammonium cupric chloride[†] crystals in a litre of water, and into 120 c.c. of this solution, contained in a beaker, add 5 grms. of the iron or steel, and digest at a gentle heat[‡] with constant stirring until complete disintegration is effected. Should the liquid become colourless, or nearly so, more of the chloride solution should be added, and on no account must it be allowed to approach boiling temperature, as this causes the silicon to acquire a condition which retards the operation of filtering. Upon complete disintegration, allow the residue, composed of combined and graphitic carbon and metallic copper, to subside, and decant off as much as possible the supernatant liquid; passing it through an asbestos filter constructed as follows:—A piece of glass tubing, ½ in. diameter and 6 in. long, is contracted at about 1 in. from one end, and this narrow portion loosely plugged with glass wool. On the top of this a layer of finely divided asbestos fibre is placed, previously ignited in a current of moist air, and wash with water as long as any of the fibre runs through. The next step is to extract the copper from the carbonaceous residue. This is accomplished by adding hydrochloric acid together with a fresh portion of the chloride solution, and digesting until the whole of the metal has dissolved. When this is effected pass the supernatant solution through the asbestos filter, throw on the residue by means of a fine jet of water, wash several times with hot hydrochloric acid, and finally with water, until a drop of the washings after acidification with nitric acid gives no opalescence with silver nitrate. The residue is now ready for combustion.

*Determination of the Total Carbon in the Crude Residue.*—Either a dry or wet method of combustion may be employed for the determination of the carbon in the crude residue. Amongst the latter is Ullgren's, the principle of which is that, upon treating the carbonaceous residue with chromic and sulphuric acids, the carbon is oxidised into carbonic acid ($CO_2$), which is weighed either directly or indirectly.



The apparatus employed is shown in Fig. 1, below. As will be seen, it consists of a small flask, A, of about ½ litre capacity, connected with a system of tubes D C E F, H containing reagents for purifying, drying, and absorbing the carbonic acid evolved. The neck of the flask is fitted with a caoutchouc cork, through which passes the stop-cock funnel B, reaching to nearly the bottom, and also a tube bent at right angles, connected with the tubes K M. The asbestos filter containing the crude carbonaceous residue, obtained as above, is transferred to the flask A by inverting the filter tube in the neck and gently blowing it out, rinsing in with the smallest quantity of water possible the portions adhering to the sides. Now add to the flask about 50 c.c. of concentrated sulphuric acid, allow to cool, insert the caoutchouc cork, and connect with the system of tubes. Add 8 grms. of chromic acid crystals dissolved in a little water through the funnel B, close the stop-cock, and heat the flask gently, so regulating it as to maintain an even and constant evolution of gas. The residue is immediately attacked by the acids, carbonic acid being formed. The gas as it is evolved passes over in the tube D, containing a solution of sulphate of silver in sulphuric acid, which retains any chlorine, and from thence it bubbles through the tubes C E, containing respectively sulphuric acid and calcium chloride, where the water (moisture) is absorbed. It next enters the *previously weighed* bulb tubes F, containing a solution of caustic potash (1 part alkali in 1½ water), which almost completely absorbs the carbonic acid, but a small portion, together with some of the water of the potash solution, is carried over by the unabsorbed gas. To collect this, which would otherwise be lost, and thus occasion serious error, a weighed U-tube, H, is attached, containing in the limb nearest the potash bulb granulated soda-lime, while the other is filled with calcium chloride.

As soon as heavy white fumes appear in the body of the flask, connect the tube H with an aspirator, open the

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[*] From *Industries*, February 24, 1893.

[†] Copper sulphate may be advantageously used; we deem it preferable.

[‡] Fresenius recommends that solution be effected at ordinary temperature, as, upon warming, a small quantity of gas containing carburetted hydrogen is evolved.

pinch-cock, *z*, attached to the caoutchouc tubing at the end of the glass tube protruding through the cork in the mouth of K, which is kept closed during the first part of the operation, remove the source of heat, and draw a current of air—which will be freed from moisture and carbonic acid in passing through K M, containing respectively caustic potash and calcium chloride—through the apparatus until it is thoroughly cool, when the bulb tube F is re-weighed; any increase in weight is due to carbonic acid ($CO_2$). The tube H is likewise re-weighed at the conclusion of the experiment, and the increase of weight, if any, deducted from the *first* weight of F. Carbonic acid contains 27·27 per cent of carbon. It is obvious that the apparatus must be perfectly air-tight, and also that the chemicals employed be free from organic matter. To guard against the possibility of error through this latter source, it is advisable to perform a blank experiment with the reagents only.

*Calorimetric Determination of Combined Carbon.*—As previously stated, iron and steel may contain carbon in at least two conditions, either in the free state, or graphite carbon, as it is termed, or in chemical combination with the iron. The method just described furnishes the amount of total carbon present and leaves us altogether ignorant of the proportion present in the several conditions. And as from the amount of combined and graphitic carbon, together with other constituents, although in a less degree, contained in iron or steel, we are able to determine the suitability or otherwise of the metal for certain purposes, as also to classify it, it becomes necessary to determine the quantities present respectively in the two conditions.

The combined carbon in steel may be determined by combustion, but in the laboratories connected with iron and steel works, where a large number of estimations have to be performed during the course of the day, the method is rarely brought into requisition, as it involves both considerable time and labour. The method commonly employed is Eggertz's calorimetric test, the principle of which is that upon dissolving iron or steel containing combined carbon in nitric acid free from chlorine, a brown coloured solution is produced, varying in intensity or depths of tints in proportion to the amount contained in the metal. It is therefore a simple matter to determine by this method the combined carbon contained in any nitric acid solution of the metal by comparing with that obtained upon treating a "standard" containing a known amount of combined carbon in a precisely similar manner. Under certain conditions, and in the hands of a skilful and intelligent operator, Eggertz's test gives fairly good results, but with some classes of iron and steel it entirely fails. This is the case with specimens that have been hardened or contain over 1 per cent of carbon. It is obvious that for the carrying out of the method, standard steels, in which the combined carbon has been carefully determined by combustion, are required, and it is requisite that these should be of the same make and contain as near as possible a like amount of combined carbon as the samples under examination. Artificial coloured standards are, in our opinion, of no use whatever; and it is impossible to get accurate results by comparing a standard high in carbon with a low carbon steel.* The *modus operandi* of the calorimetric method is as follows:—Weigh out into a dry test-tube, ½ in. diameter and about 6 in. long, 0·20 grm. of the same quantity of a standard steel. To each add 5 c.c. of nitric acid, specific gravity 1·20, free from chlorine, and when all action is at an end, place the tubes in a vessel containing water kept at boiling temperature for fifteen minutes. At the end of this period the tubes are simultaneously withdrawn, any crust adhering to the inside of them being removed by causing the solution to flow over it, and placed in a vessel containing cold water.

When perfectly cold the solution of the standard steel is transferred, without loss, to a graduated tube closed at one end of 200 c.c.. divided into 1·10th c.c. capacity, the test-tube rinsed out with a little *cold* water, the washings added to the bulk of the solution, which is now diluted, until the volume occupied is a power of the percentage of combined carbon which it contained, and mixed by closing the open end of the tube with the thumb, and inverting two or three times. Supposing the standard to contain 0·35 per cent combined carbon, the solution would be diluted until the volume occupied measured 7 c.c., which is the 0·05th power of 0·35. The solution of the specimen under examination is next transferred to a tube of a like calibre and graduation as the standard; the last portion rinsed in with the least possible quantity of cold water, and the solution thoroughly mixed *without dilution*. If it be found upon comparing the colour of the two liquids, by holding the tubes side by side before a window with a piece of unglazed paper behind them, that the colour of the standard is lighter than the sample being analysed, the latter is cautiously diluted with small quantities of cold water, mixing and comparing after each fresh addition until the tints are of equal intensity. The volume in c.c. occupied by the solution of the sample—when this is obtained—multiplied by the power, of which the volume occupied by the standard is of the carbon it contains, will yield the percentage of combined carbon. If, however, upon comparing the two solutions the standard is found to be darker than the sample, the volume of the former is doubled, and only half the volume of the latter taken upon the attainment of equal tints. If the operator, upon the obtainment of equality of tints, will reverse the position of the tubes, placing the one formerly held to the right to the left, he will find in all probability that the one now held to the right will seem slightly the darker of the two. He should therefore make it a rule to hold the standard solution always to the same side, either to the right or left.

With specimens containing minute portions of combined carbon, the resulting solutions are invariably of a greenish colour. This to a certain extent may be obviated by employing half the volume of nitric acid, both for the samples and standard steel.

As the nitric acid solution of the metal obtained in the colorimetric method becomes decomposed after a short exposure to the light and atmosphere, it is not possible to make the standard solution serve for a whole day's work, a fresh standard must be prepared with each batch of determinations. Even were this admissible, the fact that, to obtain anything like accurate results, the conditions, as regards temperature, &c., under which the solution is effected must be *precisely* similar, would render it impracticable. This entails both time and labour, which some chemists obviate by employing permanent standards composed of burnt sugar, metallic salts, burnt coffee, &c. We strongly condemn this practice on account of the very necessary condition above stated being totally ignored. Stead has devised a method for the calorimetric determination of combined carbon, in which 1 grm. of the metal is dissolved in 12 c.c. of nitric acid 1·20 specific gravity, diluted with 30 c.c. of water, 13 c c. of a caustic soda solution 1·27 specific gravity added, which results in the depth of tint being considerably intensified, filtered through a dry filter, and compared, in a special form of chromometer, with the colour of a standard steel treated in a precisely similar manner. A chromometer for the calorimetric determination of carbon has also been devised by Mr. C. H. Ridsdale, full particulars of which appeared in the *Journ. Soc. Chem. Ind.*, vol. vii., p. 70—73.

The colour test for carbon is only applicable to steel when produced under like conditions. Hammered steel frequently shows more combined (colour test) carbon than is originally contained in the ingot after hardening or drawing out the ingots.

In the latter there is always a portion of carbon which cannot be termed graphite, but existing in a state insensible to the colour test, and this portion is found to

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* The other constituents should also be nearly as possible present in the same proportions.

increase according to the total amount of carbon in the metal, as also the rapidity with which it is cooled. Therefore in some degree the composition of steel seems modified, like common grey iron in which the proportion of graphite is more or less in accordance with the rate of cooling. Discrepancies in the determination of combined carbon by the colour test of the same cast of steel have thus been explained.

(To be continued).

## THE USE OF THE TERM "CARBOHYDRATES."

By W. E. STONE, Ph.D., Purdue University, Lafayette, Ind.

It has frequently happened in the history of chemistry that names and terms have lost their original significance so soon as the knowledge of the bodies to which they were applied has become more extended. "Organic" chemistry is better named the "chemistry of carbon compounds"; the "aromatic" bodies have disappeared in the broader designation of benzine derivatives. In the same way it appears that we have reached, or already passed, a transition stage in the use of the term "carbohydrates." Treatises on chemistry still retain the old definition of the term, while those familiar with recent progress in this field no longer feel themselves restricted to these ancient limits. It is the purpose of this paper to consider the present status of this subject.

Von Lippmann, in his work "Die Zuckerarten und ihre Derivate," adopts Fittig's view that the carbohydrates are derived from the hypothetical heptatomic alcohol—

$$C_6H_7(OH)_7,$$

which, by loss of water, forms the simple or complex anhydrides, $C_6H_{12}O_6$ or $C_{12}H_{22}O_{11}$, known as sugars. His treatment ignores the existence of any carbohydrate with less than six carbon atoms, although he says that, with the (at that time, 1882) slight knowledge of the constitution of the carbohydrates, it was impossible to regard this definition as final and complete.

In 1888 appeared Tollens's "Handbuch der Kohlenhydrate," in which the definition of "carbohydrates" was limited strictly to the bodies composed of C, H, and O, containing six carbon atoms, or some multiple of six, and H and O in the same proportion in which they are found in water. But already Kiliani had shown that arabinose, which had long been regarded as a true carbohydrate on account of all its reactions, had really the composition $C_5H_{10}O_5$. Moreover, it had already been established that the best-known sugars, such as dextrose, levulose, galactose, and arabinose, had the constitution of aldehyds or ketones of the hexatomic, respectively pentatomic, alcohols. In anticipation, therefore, of evident progress along this line, Tollens remarks, in his Preface, that such bodies as arabinose and the impending erythrose might well be regarded as carbohydrates, but he retains the hexatomic nature as a requirement for the "true carbohydrate," and puts all non-conforming but similar bodies under the head of "den Kohlenhydraten nahestehenden Körper."

Up to this time a sort of understanding had prevailed that the carbohydrates were exclusively products of natural forces. It had also been noted that these bodies gave certain reactions, which were also presented as a basis for the classification given.

These reactions, as stated by Tollens, are—

1. Reduction of alkaline metallic solutions.
2. Rotation of polarised light.
3. Subject to alcoholic fermentation by yeast.
4. Formation of levulinic acid.
5. Formation of characteristic compounds with phenylhydrazin.
6. Certain colour reactions.
7. Solubility, either before or after hydrolysis.
8. Decomposition by heat.

All of which hold strictly true for the hexatomic carbohydrates. This classification was probably as liberal as the state of knowledge at that time would justify.

But this classification is evidently arbitrary, and ought not to have weight in comparison with any classification based on chemical constitution. If a similar constitution can be proven for a series of bodies, the fact that they respond to certain reactions will only be additional proof of their relationship. Such reactions must, of course, be general in their nature, while special reactions will only serve to characterise individuals. In this way the class of carbohydrates must eventually include only bodies of certain constitution, while the characteristic reactions will be limited to a smaller number, of more general application. A similar development has taken place in the manner of classifying the hydrocarbons, alcohols, acids, glycerides, &c.

Of the carbohydrates conforming to the old definition, dextrose, levulose, galactose, and mannose are types. They respond to the reactions given, and have been found to possess the constitution of ketones or aldehyds of the hexavalent alcohol, $C_6H_{14}O_6$. But we know two bodies of the formula $C_5H_{10}O_5$, arabinose and xylose, which are also aldehyd alcohols, and which give the same reactions as their homologues, with the exception of fermentation and the formation of levulinic acid. Again, we know an aldehyd of the tetratomic alcohol erythrit, called erythrose, of the formula $C_4H_8O_4$, which responds to the same general reactions as its homologues. Glycerose, $C_3H_6O_3$, has also been studied, and found to correspond to the others of the series in constitution and general reactions. It is even fermentable with yeast, like the regular carbohydrates, which shows this to be an intermittent reaction when applied to an homologous series. Beginning again with the group $C_6H_{12}O_6$, we find that there have been prepared synthetically three other homologues representing aldehyds, respectively of the hept-, oct-, and nonatomic alcohols. These also respond to the general reactions given, except that they do not form levulinic acid. Heptose and octose do not ferment, but nonose, with its multiple of three carbon atoms, is fermentable.

It is no argument against the carbohydrate nature of these bodies to say that they do not occur in nature, since two of the hexoses (galactose and mannose) have never been found free, but are only known as derivatives of certain natural products. In this respect they are on precisely the same footing as arabinose, xylose, erythrose, and glycerose.

It appears, therefore, that we have an homologous series of aldehyd or ketone alcohols of the general formula $C_nH_{2n}O_n$ with these common properties:—1, sweet to the taste; 2, optically active; 3, reducing alkaline metallic solutions; 4, yielding with phenyl hydrazin characteristic crystallinic compounds. Other reactions, such as great solubility, decomposition by heat, and colour reactions, are less characteristic, although possessed in common. Those containing three, or multiples of three, carbon atoms undergo alcoholic fermentation with yeast, and this periodical reaction seems an additional argument for their common nature. Individually they yield, when heated with strong acids, characteristic derivatives; for instance, the pentoses yield furfurol, the hexoses levulinic acid; others have not been carefully studied in this direction.

Following are the members of this homologous series which are known, although several additional isomers are possible:—

Triose, $C_3H_6O_3$.—Glycerose.
Tetrose, $C_4H_8O_4$.—Erythrose.
Pentose, $C_5H_{10}O_5$.—Arabinose, xylose.
Hexose, $C_6H_{12}O_6$.—Dextrose, levulose, galactose, mannose, all in isomeric forms.
Heptose, $C_7H_{14}O_7$.—Heptose.
Octose, $C_8H_{16}O_8$.—Octose.
Nonose, $C_9H_{18}O_9$.—Nonose.

By the definition of carbohydrates, now extant, only the hexoses are included. It is the purpose of this paper to propose the extension of this term to all members of the homologous series, on the basis of a common constitution, *viz.*, as aldehyds or ketones of the normal polyatomic alcohols of the aliphatic series. As characteristic properties of all these, must follow their behaviour toward polarised light, toward alkaline metallic solutions, and toward phenylhydrazin.

Such a classification would exclude the bodies of the cellulose group, of which there are many, more or less well defined. But it is not yet evident that they possess a constitutional relation to the bodies under discussion, and have certainly no claim to be classed with the aldehyd or ketone alcohols because convertible into them.

As for the disaccharides of the hexoses, to which belong sucrose, lactose, &c., if it be true, as supposed, that they are anhydrides or ether-like forms of the hexoses, then they are entitled to a place among carbohydrates as derivatives or modifications of the same.

E. Fischer proposes to apply the name "sugars" to all the members of this homologous series, to which he has lately added the glycol-aldehyd $C_2H_4O_2$ as the simplest possible example. The popular conception of the properties of a sugar are not, however, easily reconciled with the properties of some of these bodies, while "carbohydrates" at least possess some reference to their empirical composition. With regard to glycol-aldehyd, moreover, its optical inactivity would exclude it from the list under the conditions here proposed, although its constitution undoubtedly satisfies the requirements.—*Science.*

## THE PERIODIC ARRANGEMENT OF THE ELEMENTS.

By P. J. F. RANG.

The general plan of the Table is to arrange the elements in their respective series, so that all the allied elements ahould come in the same vertical row. The Table has been divided into four groups, A, B, C, and D, whereof the end group A contains the strongest positive elements, and the other end group D the strongest negative elements. In the centre group B are the elements with high melting points; they are all remarkable for their molecular combinations. At one side of this group are the anhydro combinations; at the other side are the amin, carbonyl, and cyanogen combinations; in the other centre group, C, are the heavy metals that have low melting points. If groups A and D be split up vertically in respectively three and two parts, the Table presents seven vertical groups, and horizontally seven more or less complete series. Each group in each of the series 2 and 3 are represented with one element. The octave appears also both horizontally and vertically in the Table; this is in conformity with a great scientific authority, who tells us that the octave is extended over all nature, and that it is to be found in two diametrically different directions. The atomic weight of Li—the first periodic alkali element—seems also to show the octave.

Wimmerby, Sweden.

| Valence. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | | | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Series. | | | | | | | | | | | | | | | | | |
| 1. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | H | .. | .. | .. | .. |
| 2. | Li | Be | B | C | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | N | O | F |
| 3. | Na | Mg | Al | Si | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | P | S | Cl |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Ni | Co | Cu | Zn | Ga | Ge | As | Se | Br |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | .. | Ru | Rh | Pd | Ag | Cd | Tn | Sn | Sb | Te | I |
| 6. | Cs | Ba | Di | .. | Ta | W | .. | Os | Tr | Pt | Au | Hg | Tl | Pb | Bi | .. | .. |
| 7. | .. | Ms | .. | Th | .. | U | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| Group | 1. | 2. | 3. | 4. | | | | | | | 5. | | | | | 6. | 7. |
| | | A. | | B. | | | | | | | C. | | | | | D. | |

Di here represents all the triads that are between Ba and Ta. H may not be exactly in its true place, still it cannot be very far from it.

## TECHNICAL ESTIMATION OF LEAD.

By ALBERT H. LOW.

Provide three wash-bottles containing the following solutions respectively:—

Distilled water, or, at least, chlorine-free water.

Dilute sulphuric acid. One part C. P. acid to 9 parts chlorine-free water.

Chloride of ammonium. Make a saturated solution of the commercial chloride in common water: transfer this to the wash-bottle as required, and heat to boiling for use.

Treat 1 grm. of the ore in a covered Griffin beaker, of about 150 c.c. capacity, with 10 c.c. of a mixture of equal parts strong pure nitric acid and water. Heat carefully until the ore is pretty well decomposed, and then add 10 c.c. of pure strong sulphuric acid, and heat strongly until all the nitric acid is expelled and the sulphuric acid is boiling freely. This is best done over a small naked flame, taking care that the flame does not touch the beaker above the liquid. A 250 c.c. flask has some advantages over a beaker for this decomposition, but is harder to wash out subsequently. Cool and add 10 c.c. of the above dilute sulphuric acid. Then add 2 grms. of Rochelle salt, roughly weighed, or even guessed at. When this is dissolved add 40 c.c. of distilled water, and heat to boiling. Allow to stand and settle two minutes, and then filter and wash with the dilute sulphuric acid. Now spread the filter out carefully on a watch-glass, and wash the contents back into the beaker with a stream of the boiling hot chloride of ammonium solution. Heat the beaker again until all the sulphate of lead has dissolved, adding more chloride of ammonium if necessary. Again filter, receiving the filtrate in a clean flask, and wash the filter thoroughly with the hot chloride solution. Small amounts of sulphate of lead may be easily dissolved upon the original filter, without removing from the funnel, by simply washing with the hot chloride solution. Place in the filtrate three pieces of sheet aluminum, each about one-sixteenth of an inch thick by five-eighths of an inch wide and an inch and three-quarters long. The aluminum should be the purest obtainable, as the commercial article leaves an appreciable residue of silicon on dissolving. Heat the contents of the flask to boiling. If the bulk of the filtrate has been kept down to 75 or 100 c.c., the lead will be completely precipitated with five minutes' boiling. Remove from the heat, and shake the mixture around to collect the lead. The aluminum should appear clean, with but little lead adhering to it. Fill the flask with cold water, and transfer the entire contents to a large casserole. Wash the lead twice by decantation, and, after filling up the casserole the third time, remove the aluminum with the hand, rubbing off any adhering lead under water. Again decant and then rinse the lead into a small porcelain dish. Pour off the water and, with an agate pestle, collect the lead as nearly as practicable into one piece, and press it into a thin hard sheet. Wash this once or twice with distilled water and then with alcohol. Dry the lead carefully, which should not cause any oxidation whatever, and then brush it into the scale-pan and weigh. The lead is practically free from silver, gold, copper, antimony, bismuth, arsenic, &c. A deduction of 3 per cent is a fair allowance for arriving at the fire assay of a pure ore of the same grade. As but little of the aluminum is dissolved, the same pieces may be used repeatedly.—*Journal of Analytical and Applied Chemistry*, vi., No. 12.

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## NOTICES OF BOOKS.

*Diseases Incident to Workpeople in Chemical and other Industries.* An Address Delivered before the Chemical and Physical Society of University College, London. By Watson Smith. London: Eyre and Spottiswoode, 1893. 8vo., 34 pp.

This judicious and timely pamphlet is substantially a review of Dr. J. T. Arlidge's work, "The Hygiene, Diseases, and Mortality of Occupations," and it has been called forth by certain ill-judged and sensational notices of the same book which have been contributed to daily papers by certain unqualified writers.

We do not, of course, even if we had the power, object to the discussion of technical and sanitary questions in the daily papers. On the contrary, we consider it a good feature, since hygienic evils and their remedies will thus be brought under the notice of thousands of persons to whom the scientific, medical, and technical journals are sealed books.

But we think the public has every right to demand that such subjects should be handled only by experts, physicians, pathologists, chemists, and technologists; that all exaggeration and everything of a sensational character should be avoided, and that all attempts to make the questions subserve the purposes of faction should be rigorously excluded.

Now these essential features are conspicuous by their absence in the series of notices which have appeared in a certain morning paper. As Mr. Watson Smith puts it, "Dr. Arlidge's eminently correct and sober title is changed for the highly sensational and exaggerated one 'Death in the Workshop.'"

In the same morning paper we read: "For the most part Dr. Arlidge's moral is to exhibit the avoidable shortening of the lives of our brothers and sisters for the simple reason that *it suits* (!) certain manufacturers to produce their wares under conditions which make healthy living impossible, and that it has not yet occurred to the State to step in and prevent them." What would the newspaper writer just quoted think if told that it *suits* certain journalists to delude the British workman into the belief that he is ill-treated for the convenience of the manufacturer? If such journalists were really acquainted with the facts of the case they would know that the workman obstinately resists every improvement which might prolong his life. They hold, as Mr. Watson Smith tells us, and as we know from abundant personal observation, that "the best and only cure for any result of inhalation of chlorine gas, or dust, or acid vapour is a good wash down with rum or whiskey. The custom has thus sprung up of going to the office on such occasions when frequently money is allowed and the alcoholic is taken." This practice is, to our knowledge, no better than a superstition. If an oxide of nitrogen has been inhaled we have repeatedly found, in ourselves and others, that relief is most quickly and completely obtained by taking small sips of acetic acid as strong as it can be endured.

Without, however, venturing into the perilous region of the temperance question, we cannot refrain from quoting the authoritative utterance of Mr. A. E. Fletcher, H.M. Chief Inspector under the Alkali Acts, that "there is nothing deadly about an alkali works except the dirt and the drink."

Dr. C. O. Weber, a friend of Mr. Watson Smith, here quoted, declares that "habitual drinkers are absolutely unable to work in an atmosphere containing a quantity of aniline, which upon men of temperate habits has no effect whatever. The same is the case with the vapours of nitrobenzene." This fact may put in a stronger light the dangers of the fraudulent addition of nitrobenzene to factitious wines in order to impart to them the Burgundy flavour!

Mr. Watson Smith tells his hearers that the British chemical manufacturers, so far from seeking to obstruct sanitary improvements in their works and their processes, have in their organ, the *Journal of the Society of Chemical Industry*, a sanitary department, and "welcome all the light they can gain."

It scarcely falls within our sphere, but we may still mention that the hours of labour in the least agreeable departments of the alkali trade are short. At the establishments under the "Alkali Union" the week's work for bleaching-powder packers is thirty-four hours, and the average rate of wages 51s. 4d.

At the Widnes Alkali Works the average weekly earning for the same work is from 50s. to 60s. per week of thirty-six hours.

Some idea of the fairness of the recent newspaper criticisms of Dr. Arlidge's work may be judged from a comparison of the following statements:—Says the first of the articles on "Death in the Workshop," "Dr. Arlidge has investigated such entirely deadly facts as that the average life of the blacksmith is eighteen years." But if Dr. Arlidge is allowed to speak for himself he declares that "the occupation of a blacksmith must, on the whole, be pronounced a *healthy* one." He adds that "in commenting upon the disorders of blacksmiths the prevailing intemperate habits of these workmen must be noted."

We hope to return to a subject of so vital importance both for public health and for our national industries.

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*Soap Manufacture.* A Practical Treatise on the Fabrication of Hard and Soft Soaps; and Analytical Methods for the Determination of their Chemical Composition, together with a short account of the Materials Employed. By W. Lawrence Gadd, F.C.S. London: G. Bell and Sons.

This work forms a member of the series known as Technological Handbooks, and is calculated to be very useful at the present day.

No one can venture to assert that any new source of fatty matters or of alkalis suitable for soap making has been discovered. No new light has been thrown on the process of saponification. Yet, for all this, the trade has undergone a curious revolution. New soaps, substitutes for soaps, and adjuncts to soaps appear in all directions. The columns of the Press and the interiors of public conveyances display advertisements of these detergents, always sensational and often illustrated. Mr. Gadd would have merited well of the straightforward soap manufacturer and of the general public had he added to his work a few analyses of some of the more notorious of these recent claimants for patronage.

The first, or introductory, chapter of this work consists of a general account of the scientific principles of soap making.

In the second and third chapters we find an account of the materials as actually used. It is not encouraging to find bone-fat, kitchen-fat, and fuller's-fat ranking among the "more important" fatty substances worked up by the soap maker.

The dirty character of palm oil—the rubbish sometimes reaching 30 per cent—is duly noticed. The properties which water should and should not possess, and its purification, are next expounded. The Leblanc process for the manufacture of soda is described at a length scarcely requisite at present. We must regret that there is scope for the remark that Baumé's hydrometer is in use in some soap works. It has not a single advantage in comparison with Twaddell's instrument, and some very palpable demerits.

The analysis of soap is considered in a separate chapter, and there are, besides, instructions for the examination of the materials. The prevalent impurities in soaps, such as china-clay, magnesium silicates, &c., are touched upon, perhaps too leniently.

Upon the whole, this work may be characterised as decidedly useful and opportune. Common as soap is, a knowledge of its legitimate composition and properties is by no means common.

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*Pharmaceutical Society of Great Britain. Chemical Papers from the Research Laboratory.* Edited by Wyndham R. Dunstan, M.A., Professor of Chemistry to the Pharmaceutical Society, and Director of the Research Laboratory. Vol. I., 1892.

It is pleasant to see a professional organisation taking into consideration something worthier than instituting and multiplying examinations. The Pharmaceutical Society has formally organised a "Research Laboratory," which has now been in operation for three years, and has done no small quantity of work. The papers here inserted, which have already appeared in the *Transactions* respectively of the Royal, the Chemical, the Pharmaceutical, and the Physical Societies, are of course of special moment to pharmacists. Some, however, are more widely interesting. Among these must be placed a memoir by Prof. W. R. Dunstan on the occurrence of skatol in the vegetable kingdom. This is of general scientific value, as breaking down another of the imaginary distinctions raised between plants and animals.

The method for the purification of mercury by distillation in a vacuum, by Messrs. Dunstan and Dymond, will be welcome to all chemists—and they are now many—who require to use mercury in their researches, and who are often more or less incommoded by its impurities.

A subject of still wider interest is the so-called "Mussoenda coffee" of Réunion, which has been examined by Prof. Dunstan and found wanting. It contains neither caffeine nor any similar substance. Still the absence of caffeine would afford no guarantee against the attempt by some enterprising quack to foist the seeds upon the public as an addition to, or a "surrogate" for, coffee. Hence we are very happy to learn on the authority of the British Consul in Réunion that the shrub *Gaertnera vaginata* "yields fewer berries than the coffee tree, and would probably be more expensive."

The investigation of the artificial salicylic acid of commerce by W. R. Dunstan and O. F. C. Bloch will be a useful caution to the medical profession. Commercial salicylic acid (Kolbe's process), whether crude or dialysed, produces different physiological effects from the pure salicylic acid obtained from the oil of winter-green. The best test for the purity of salicylic acid is the determination of its melting-point, which ought to be 156·75°, and its existence in large, separate, well-defined crystals. The question is the more important as one of the ordinary impurities, paracresotic acid, is decidedly poisonous.

We hope that Mr. Dunstan will continue his useful career.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 12, March 20, 1893.

The Minister of Public Instruction has addressed to the Academy an "ampliation" of the decree by which the President of the Republic approves of the election of Sir Joseph Lister as a foreign associate.

**Preparation of a Variety of Sprouting Graphite.**—Henri Moissan.—Certain natural varieties of graphite if heated in presence of sulphuric acid or a mixture of sulphuric acid and potassium chlorate, assume the curious property of sprouting abundantly if afterwards heated to dull redness upon a plate of platinum. M. Luzi has shown that if these natural graphites are allowed to imbibe a very small quantity of monohydrated nitric acid they swell up on ignition, forming small vermiform or dendritic processes. The cause of the sprouting is the sudden liberation of a small volume of gas expanded by heat.

**Researches on Samarium.**—Lecoq de Boisbaudran.—The author submits to the Academy the results of a fractionation of Cleve's samaria by means of ammonia. The first fractions were then refractionated with oxalic acid and gave the electric ray $Z\varepsilon$ and the reversal band $Z\zeta$; the heaviest band of $Z\beta$ had collected there. The first oxalic deposit is a nearly white earth, which does not show the reversal $Z\beta$; the earth of the tailings which is decidedly yellow gives $Z\beta$. The reversal spectra, Sm and $Z\zeta$, and the electric rays $Z\varepsilon$, have approximately the same intensity in the oxalic headings and tailings. I find that $Z\varepsilon$ and $Z\zeta$ are more distinct in the ammoniacal headings than in the centre or the tailings. The three bands Sm are also decidedly more marked in the ammoniacal headings than in the centre, which, however, does not contain an appreciable quantity of any earth other than Sm. As far as the indigo of the spectrum, the absorption Sm appears constant in the ammoniacal headings, centres, and tailings. M. Demarçay has undertaken a photographic examination of the absorption in the violet and the ultra-violet. It is remarkable that my prolonged fractionations have not yielded a product giving in HCl $Z\zeta$ decidedly stronger than the orangée Sm. Mr. Crookes has also not obtained his anomalous ray very intense. I think that the band $Z\zeta$ and the anomalous ray are closely related. They are seen with substances rich in Sm, and increase when the three bands of Sm, especially the orange, tend to decrease. In very samariferous yttria, the so-called anomalous ray has the $\lambda$ indicated by Mr. Crookes. In samariferous gadolinia, lanthana, and terbia, its position varies.

**Election of a Correspondent for the Chemical Section vice the late M. Alria.**—Sir H. Roscoe obtained 28 votes as against 17 given to Prof. Cannizzaro and 1 to Prof. Mendeleeff, out of a total of 47 votes. Sir H. Roscoe was therefore proclaimed duly elected.

**Electric Laboratory Crucible with a Directing-Magnet.**—E. Ducretet and L. Lejeune.—This apparatus cannot be intelligibly described without the accompanying cut.

**Phenomenon of Dissociation of Sodium Chloride if Heated in Contact with a Septum of Porous Earth.**—M. de Sanderval.—If we heat a tube of porous earth in an external atmosphere of sodium chloride in the state of vapour mixed with dry air, the tube becomes filled with chlorine. The exterior atmosphere of sodium chloride contains but little free chlorine. There is here a chemical reaction between the sodium chloride and the silica of the tube and also dissociation by heat. The apparatus is an earthenware tube encased in a wider porcelain tube, the whole placed in a tube furnace. The sodium chloride is deposited in the annular space between the two tubes, where it is converted into vapour. By leaning the furnace lengthwise we obtain a draught sufficient for introducing the necessary current of air.

**Hydurilic and Desoxyamalic Acids.**—C. Matignon.—A thermo-chemical paper, not susceptible of useful abstraction, and not of sufficient importance for insertion *in extenso.*

**Action of Cotton upon Sublimate absorbed from Dilute Solutions.**—Leo Vignon.—The mercury absorbed takes three distinct conditions: one part is soluble in cold water, a second part is soluble in cold acidulated water (10 per cent HCl at 22°), and a third part may be dissolved by boiling solutions of common salt (10 per cent NaCl). From the author's experiments it appears that (1) bleached cotton steeped in dilute solutions of sublimate fixes mercuric oxide in excess in preference to the hydrochloric acid. The fixation may exceed 3(HgO) to 1(HCl). (2) This cotton, if dried at the ordinary temperature and then after some days steeped in water, only gives off a part of its mercury in the state of $HgCl_2$ and its hydrochloric acid, whilst it retains HgO and $Hg_2Cl_2$. The calomel is probably formed by the reaction—

$$HgCl_2 + HgO = Hg_2Cl_2 + O,$$

the oxygen being absorbed by the cellulose and converting it into oxycellulose. (3) On exposure for some hours to a temperature of 60°, the mercuric chloride and oxide diminish, and the proportion of calomel increases.

**The Use of Ruthenium Red in Microscopic Morphology.**—Louis Mangin.—The colour discovered by M. Joly in his researches on the ruthenium ammoniacal compounds, rivals the most brilliant coal-tar pigments by its tinctorial intensity. The author has observed that ruthenium red is the best reagent for the pectic compounds, which are always associated with cellulose in young tissues and in old tissues which have not been modified by foreign matters. It is the only reagent for the transformation products of the pectic compounds, *i.e.*, the majority of gums and mucilages.

### *Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxi., No. 2.

**The Mines and the Metallurgy of Nickel.**—All the nickel of commerce is at present obtained from two very extensive deposits,—the one in New Caledonia, and the other at Sudbury, in the province of Ontario, in Canada. The Sudbury ore is remarkable for its freedom from arsenic, and it contains only ½ per cent of cobalt. The nickel ore of New Caledonia is a double nickel and magnesium silicate containing from 8 to 10 per cent of nickel. Its specific gravity is from 2·3 to 2·8, and its colour a pale grey. It contains neither cobalt nor arsenic, and is accompanied by chrome-iron and talc. The Sudbury ore is a sulphide, containing from 2 to 4 per cent of nickel. The fumes given off during the roasting process completely destroy vegetation in the district.

**Gold in Finland.**—During the eighteen years of working, from 1870 to 1887, the quantity of fine gold obtained has amounted to 321·3 kilos. The sand washed has reached a yearly average of 342 cubic metres.

### *Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 6.

At the meeting of the Society held on March 1, the President announced the new regulations resolved on by the Council concerning "sealed papers," which may, it seems, in some cases lie for twenty-five years unopened, or may be withdrawn by the authors at the end of ten or of twenty years.

**Researches on Thallium. New Determination of its Atomic Weight.**—Charles Lepierre.—From the *Comptes Rendus.*

**A New Oxalylmalonic Diureide.**—C. Matignon.—The composition of this substance is expressed by the formula $C_7O_6N_4H_6$. If heated to 105° it loses 1 mol. of water, and is then apparently anhydrous. It is decomposed by water into barbituric and parabanic acids.

### *Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 85.

According to Lindot, phosphoric acid equivalent to 2000 tons calcium phosphate is yearly withdrawn from use and locked up, so to speak, in the cemeteries in the bones of the dead.

### *Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 2, 1893.

**Gas-Volumetric Determination of Organic Acids and of Iodic Acids.**—H. Kux.—This paper does not admit either of abstraction or of full insertion on account of its length and the number of tables which it contains.

**Microchemical Detection of Sulphur. Notice on the Use of Gaseous Reagents, especially Bromine Vapour, in Microchemical Analysis.**—F. Emich.—This paper will be inserted in full.

**Chemico-Legal Examination of Stains suspected to be Blood.**—H. Struve.—This paper will be inserted in full.

**Iodine Addition Method.**—F. Gautter.

**New Method for Determining the Iodine-Number in Fats and Oils.**—F. Gautter.—Both these papers will be inserted in full.

**Determination of Potassium.**—E. W. Hilgard.—The weighing of potassium platinum chloride certainly gives good results in experienced hands, especially in the Gooch crucible. Still, the weighing of filters is always a rather critical operation, and may give rise to variable results, according to the experience of the operator and the moisture of the air. I therefore prefer to weigh the reduced platinum, which I effect as follows:—I use a small platinum crucible, reserved exclusively for this use. The inside for about half its height from the bottom, is coated with a layer of platinum sponge, which may be effected in a quarter of an hour by carefully decomposing a few decigrms. of the platinum double salt, inclining the crucible sideways and turning it occasionally round. The platinum sponge promotes the decomposition of the double salt so much that it may be quickly and quietly completed at a relatively moderate heat, the cover being kept in its place. When completed, the crucible is heated strongly for some time in order to render the platinum sponge so coherent that on subsequent washing by decantation no traces may rise to the surface and be lost. The chief part of the potassium chloride is volatilised during the last ignition. When cold, two drops of concentrated hydrochloric acid are let fall into the crucible. If on heating there appears the slightest yellowness, the acid is evaporated off and the ignition repeated, adding a little oxalic acid. In the majority of cases the yellowness springs from a trace of ferric chloride, and therefore reappears after the second ignition on the addition of hydrochloric acid. It is then washed by repeated decantation, raising the crucible to ebullition by applying heat to one side. The product is ignited and weighed. The results are nearly always rather lower than those obtained by weighing the double salt, and the acid washings first poured off contains as a rule traces of earths, and almost without exception a little sodium chloride. No correction for the ash of the filter is admissible.

**Absorption- and Washing-Apparatus.**—C. Mann.—Requires the accompanying illustration.

## MEETINGS FOR THE WEEK.

Monday, 17th.—Medical, 8.30.
— Society of Arts, 8. "Some Masters of Ornament," by Lewis Foreman Day. (Cantor Lectures).
Tuesday, 18th.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "Symbolism in Ceremonies, Customs, and Art," by John Macdonell, LL.D.
— Society of Arts, 8. "The Philippine Islands," by H. A. McPherson.
Wednesday, 19th.—Meteorological, 7.
— Microscopical, 8.
— Society of Arts, 8. "Some Economic Points in connection with Electricity Supply," by Gisbert Kapp.
Thursday, 20th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
— Chemical, 8. "Contribution to the Chemistry and Physiology of Foliage Leaves," by Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D. "The Interaction of Alkali Cellulose and Carbon Bisulphide—Cellulose Thio-carbonates," by C. F. Cross, E. J. Bevan, and C. Beadle. And other papers.
Friday, 21st.—Royal Institution, 9. "Possible and Impossible Economies in the Utilisation of Energy," by Prof. A. B. W. Kennedy, F.R.S.
— Quekett Club, 8.
Saturday, 22nd.—Royal Institution, 3. "Some Applications of Electricity to Chemistry," by James Swinburne, M.Inst.E.E. (The Tyndall Lectures).

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*The following appendix has been written upon the same lines as in former editions, save that it has been enlarged, and in reality now constitutes a treatise on the chemical substances occurring in the animal body. As in former editions it is entirely the work of Dr. A. Sheridan Lea. The references given, though extensive, are not intended to be exhaustive. An effort has been made to make the references to recent works as complete as possible, other references are to papers, which themselves give full references, and will therefore serve as a guide to literature of the subject; and some have been inserted in order to inform the student of the dates at which important results were first described."* —From the Preface.

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THE CHEMICAL NEWS.
Vol. LXVII., No. 1743.

### ON THE

# DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

In former communications (*Roy. Soc. Proc.*, February, 1888; February, 1892) I have described the arrangements by which I determined the ratio of densities of oxygen and hydrogen (15·882). For the purpose of that work it was not necessary to know with precision the actual volume of gas weighed, nor even the pressure at which the containing vessel was filled. But I was desirous before leaving the subject of ascertaining not merely the relative, but also the absolute, densities of the more important gases, that is, of comparing their weights with that of an equal volume of water. To effect this it was necessary to weigh the globe used to contain the gases when charged with water, an operation not quite so simple as at first sight it appears. And, further, in the corresponding work upon the gases, a precise absolute specification is required of the temperature and pressure at which a filling takes place. To render the former weighings available for this purpose, it would be necessary to determine the errors of the barometers then employed. There would, perhaps, be no great difficulty in doing this, but I was of opinion that it would be an improvement to use a manometer in direct connection with the globe, without the intervention of the atmosphere. In the latter manner of working, there is a doubt as to the time required for full establishment of equilibrium of pressure, especially when the passages through the taps are partially obstructed by grease. When the directly connected manometer is employed, there is no temptation to hurry from fear of the entrance of air by diffusion, and, moreover (Note A), the time actually required for the establishment of equilibrium is greatly diminished. With respect to temperature, also, it was thought better to avoid all further questions by surrounding the globe with ice, as in Regnault's original determinations. It is true that this procedure involves a subsequent cleaning and wiping of the globe, by which the errors of weighing are considerably augmented; but as it was not proposed to experiment further with hydrogen, the objection was of less force. In the case of the heavier gases, unsystematic errors of weighing are less to be feared than doubts as to the actual temperature.

In order to secure the unsystematic character of these errors, it is necessary to wash and wipe the working globe after an exhaustion in the same manner as after a filling. The dummy globe (of equal external volume, as required in Regnault's method of weighing gases) need not be wiped merely to secure symmetry, but it was thought desirable to do so before each weighing. In this way there would be no tendency to a progressive change. In wiping the globes the utmost care is required to avoid removing any loosely attached grease in the neighbourhood of the tap. The results to be given later will show that, whether the working globe be full or empty, the relative weights of the two globes can usually be recovered to an accuracy of about 0·3 m.grm. As in the former papers, the results were usually calculated by comparison of each "full" weight with the mean of the immediately preceding and following empty weights. The balance and the arrangements for weighing remained as already described.

*The Manometer.*

The arrangements adopted for the measurement of pressure must be described in some detail, as they offer several points of novelty. The apparatus actually used would, indeed, be more accurately spoken of as a manometric gauge, but it would be easy so to modify it as to fit it for measurements extending over a small range.

The object in view was to avoid certain defects to which ordinary barometers are liable, when applied to absolute measurements. Of these three especially may be formulated:—

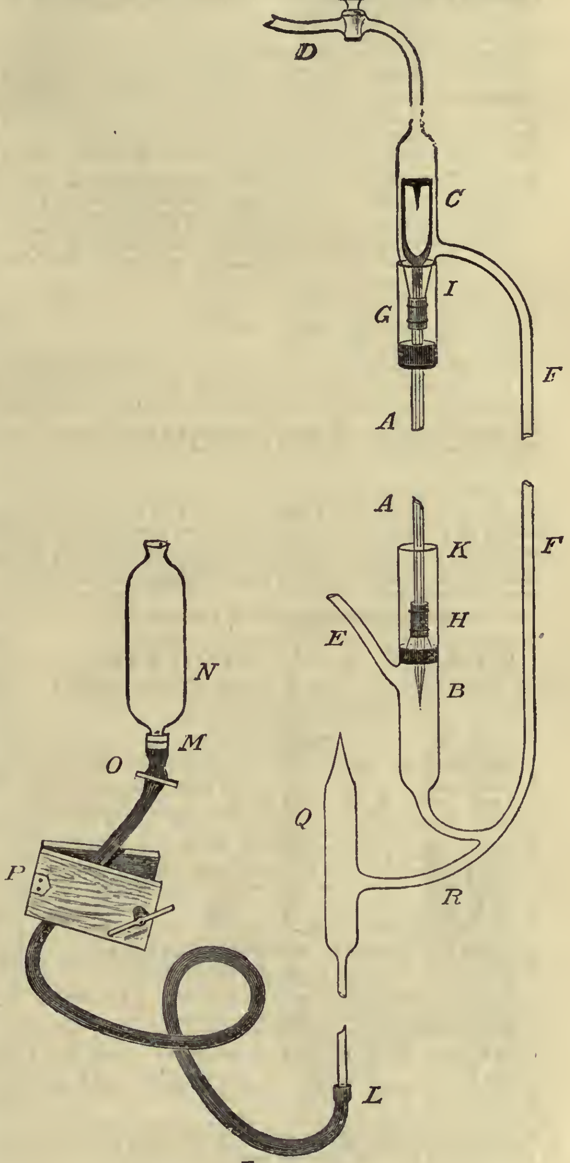

Fig. 1.

*a*. It is difficult to be sure that the vacuum at the top of the mercury is suitable for the purpose.
*b*. No measurements of a length can be regarded as satisfactory in which different methods of reading are used for the two extremities.
*c*. There is necessarily some uncertainty due to irregular refraction by the walls of the tube. The apparent level of the mercury may deviate from the real position.

---

* A Paper read before the Royal Society.

*d*. To the above may be added that the accurate observation of the barometer, as used by Regnault and most of his successors, requires the use of a cathetometer, and expensive an not always satisfactory instrument.

The guiding idea of the present apparatus is the actual application of a measuring rod to the upper and lower mercury surfaces, arranged so as to be vertically superposed. The rod AA, Fig. 1, is of iron (7 m.m. in diameter), pointed below B. At the upper end, C, it divides at the level of the mercury into a sort of fork, and terminates in a point similar to that at B, and, like it, directed downwards. The coincidence of these points with their images reflected in the mercury surfaces, is observed with the aid of lenses of about 30 m.m. focus, held in position upon the wooden framework of the apparatus. It is, of course, independent of any irregular refraction which the tube may exercise. The verticality of the line joining the points is tested without difficulty by a plumb-line.

The upper and lower chambers, C, B, are formed from tubing of the same diameter (about 21 m.m. internal). The upper communicates through a tap, D, with the Töppler, by means of which a suitable vacuum can at any time be established and tested. In ordinary use, D stands permanently open, but its introduction was found useful in the preliminary arrangements and in testing for leaks. The connection between the lower chamber B and the vessel in which the pressure is to be verified takes place through a side tube, E.

The greater part of the column of mercury to which the pressure is due is contained in the connecting tube, FF, of about 3 m.m. internal diameter. The temperature is taken by a thermometer whose bulb is situated near the middle of FF. Towards the close of operations the more sensitive parts are protected by a packing of tow or cotton-wool, held in position between two wooden boards. The anterior board is provided with a suitable glass window, through which the thermometer may be read.

It is an essential requirement of a manometer on the present plan that the measuring rod pass air-tight from the upper and lower chambers into the atmosphere. To effect this the glass tubing is drawn out until its internal diameter is not much greater than that of the rod. The joints are then made by short lengths of thick walled indiarubber, H G, wired on and drowned externally in mercury. The vessels for holding the mercury are shown at I K. There is usually no difficulty at all in making perfectly tight joints between glass and tubes in this manner; but in the present case some trouble was experienced in consequence apparently of the imperfect approximation between the *iron* and the mercury. At one time it was found necessary to supplement the mercury with vaseline. When tightness is once obtained, there seems to be no tendency to deterioration, and the condition of things is under constant observation by means of the Töppler.

The distance between the points of the rod is determined under microscopes by comparison with a standard scale, before the apparatus is put together. As the rod is held only by the rubber connections, there is no fear of its length being altered by stress.

The adjustment of the mercury (distilled in a vacuum) to the right level is effected by means of the tube of black rubber, L M, terminating in the reservoir, N. When the supply of mercury to the manometer is a little short of what is needed, the connection with the reservoir is cut off by a pinch-cock at O, and the fine adjustment is continued by squeezing the tube at P between a pair of hinged boards, gradually approximated by a screw. This plan, though apparently rough, worked perfectly, leaving nothing to be desired.

It remains to explain the object of the vessel shown at Q. In the early trials, when the rubber tube was connected directly to R, the gradual fouling of the mercury surface, which it seems impossible to avoid, threatened to interfere with the setting at B. By means of Q, the mercury can be discharged from the measuring chambers, and a fresh surface constituted at B as well as at C.

The manometer above described was constructed by my assistant, Mr. Gordon, at a nominal cost for materials; and it is thought that the same principle may be applied with advantage in other investigations. In cases where a certain latitude in respect of pressure is necessary, the measuring rod might be constructed in two portions, sliding upon one another. Probably a range of a few millimetres could be obtained without interfering with the indiarubber connections.

The length of the iron rod was obtained by comparison under microscopes with a standard bar, R, divided into millimetres. In terms of R the length at 15° C. is 762·248 millimetres. It remains to reduce to standard millimetres. Mr. Chaney has been good enough to make a comparison between R and the iridio-platinum standard metre, 1890, of the Board of Trade. From this it appears that the metre bar R is at 15° C. 0·3454 m.m. too long; so that the true distance between the measuring points of the iron rod is at 15° C.—

$$762{\cdot}248 \times 1{\cdot}0003454 = 762{\cdot}511 \text{ m.m.}$$

*Connections with Pump and Manometer.*

Some of the details of the process of filling the globe with gas under standard conditions will be best described later under the head of the particular gas; but the general arrangement and the connections with the pump and the manometer are common to all. They are sketched in Fig. 2, in which S represents the globe, T the inverted bell-glass employed to contain the emveloping ice. The connection with the rest of the apparatus is by a short tube, U, of thick rubber, carefully wired on. The tightness of these joints was always tested with the aid of the Töppler, X, the tap, V, leading to the gas generating apparatus being closed. The side tube at D leads to the vacuum chamber of the manometer, while that at E leads to the pressure chamber, B. The wash out of the tubes, and in some cases of the generator, was aided by the Töppler. When this operation was judged to be complete, V was again closed, and a good vacuum made in

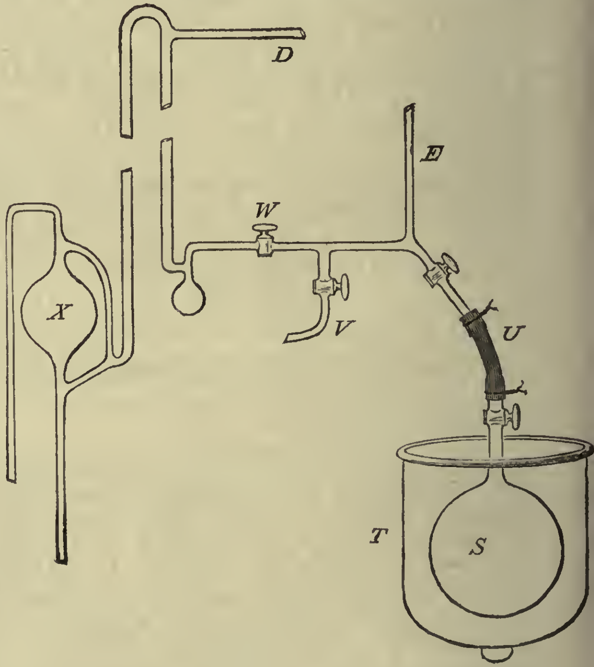

Fig. 2.

the parts still connected to the pump. w would then be closed, and the actual filling commenced by opening v, and finally the tap of the globe. The lower chamber of the manometer was now in connection with the globe, and through a regulating tap (not shown) with the gas-generating apparatus. By means of the Töppler, the vacuum in the manometer could be carried to any desired point. But with respect to this a remark must be made. It is a feature of the method employed (due to von Jolly) that the exhaustions of the globe are carried to such a point that the weight of the residual gas may be neglected, thus eliminating errors due to a second manometer reading. There is no difficulty in attaining this result, but the delicacy of the Töppler employed as a gauge is so great that the residual gas still admits of tolerably accurate measurement. Now in exhausting the head of the manometer it would be easy to carry the process to a point much in excess of what is necessary in the case of the globe, but there is evidently no advantage in so doing. The best results will be obtained by carrying both exhaustions to the *same* degree of perfection.

At the close of the filling the pressure has to be adjusted to an exact value, and it might appear that the double adjustment required (of pressure and of mercury) would be troublesome. Such was not found to be the case. After a little practice the manometer could be set satisfactorily without too great a delay. When the pressure was nearly sufficient, the regulating tap was closed, and equilibrium allowed to establish itself. If more gas was then required, the tap could be opened momentarily. The later adjustments were effected by the application of heat or cold to parts of the connecting tubes. At the close, advantage was taken of the gradual rise in the temperature which was usually met with. The pressure being just short of what was required, and v being closed, it was only necessary to wait until the point was reached. In no case was a reading considered satisfactory when the pressure was changing at other than a very slow rate. It is believed that the comparison between the state of things at the top and at the bottom of the manometer could be effected with very great accuracy, and this is all that the method requires. At the moment when the pressure was judged to be right, the tap of the globe was turned, and the temperature of the manometer was read. The vacuum was then verified by the Töppler.

(To be continued).

## DETERMINATION OF THE ALKALIS IN SILICATES.

By ALBERT H. LOW.

The following scheme is given more as a suggestion than as a description of a well-established method. The author had occasion to make some alkali determinations in a hurry, without great regard to extreme accuracy. J. Lawrence Smith's method was out of the question, as all the carbonate of calcium at hand was too impure to be available. A consideration of the fact that in the author's method for zinc (described in the *Journal of Analytical and Applied Chemistry*, Sept., 1892) all the zinc is extracted from a dried residue containing the substances from which it is ordinarily difficult to effect a good separation, led to the idea that a similar scheme might be as successfully applied to the case of the alkalis. The following method was then devised and tried with satisfactory results. If the bulks of the various filtrates, &c., are kept as small as possible, and the evaporations conducted with care over direct heat, the time required is considerably less than for Smith's method.

Treat one grm. of the finely-powdered silicate by warming gently with pure strong hydrofluoric acid and a little sulphuric acid in a 100 c.c. platinum dish until decomposition is complete. Evaporate to dryness, and heat until the fumes of sulphuric acid have nearly ceased coming off. Cool, and add a little ammonia water, and boil. See that a good disintegration is effected. Filter, washing with a little hot water. Acidify the filtrate strongly with hydrochloric acid, and add as small an excess as practicable of chloride of barium solution. Heat to boiling and filter, washing with hot water. Evaporate the filtrate to dryness in platinum, and ignite gently to expel ammonium salts. Cool, add a little carbonate of ammonium and ammonia water, boil, and filter, washing with hot water. Evaporate the filtrate to dryness in a weighed platinum dish. This gives the combined chlorides which are separated in the usual manner.

As the author had but little time to investigate as to the accuracy of this method, he sent a description to Dr. W. F. Hillebrand, of the U.S. Geological Survey at Washington, with the request that it be compared with the method in use. Dr. Hillebrand kindly complied and sent the following figures as the results of his analyses of two different samples of rock:—

| | No. I. Per cent. | | No. II. Per cent. | |
|---|---|---|---|---|
| | $K_2O$. | $Na_2O$. | $K_2O$. | $Na_2O$. |
| Smith's method .. .. | 1·95 | 4·09 | 0·32 | 3·53 |
| Low's ,, .. .. | 1·91 | 4·10 | 0·35 | 3·55 |

Dr. Hillebrand suggests that his results by Low's method may be a trifle high, owing to the presence of a trace of potassium permanganate in his hydrofluoric acid, and, on the other hand, a trifle low from the retention of alkali by magnesia, the two errors counterbalancing. Pure hydrofluoric acid is, however, easily obtained, and the error due to magnesia might possibly be avoided by using carbonate of ammonium in the original extraction. *Journal of Analytical and Applied Chemistry*, vi., No. 12.

## ON THE PURIFICATION OF WATER USED FOR STEAM-BOILERS.*

By R. JONES, Ph.D.

(Concluded from p. 173).

The following example illustrates the use of carbonate of soda for the purpose of water purification. A boiler under my supervision is fed with water from the Elbe, treated by warming with carbonate of soda solution and passing through a filter-press. Our system is neither Dehne's, nor Klein, Schanzlin, and Becker's. A filter-press that had formerly been used for a different purpose was unearthed and requisitioned, and for a warming-vessel we made use of a small steam-boiler, for which we had no other use. The apparatus was put together by our own workmen, the only cash expended being twelve marks for a small graduated cock obtained from Klein, Schanzlin, and Becker's for regulating the flow of the soda solution. The apparatus, notwithstanding its cheapness, works to our complete satisfaction, and a similar one could easily be fitted up in any other works. The consumption of carbonate of soda amounts to 2·5 kilos. a day. We add just so much solution as suffices after filtration to produce a distinct red colour with phenolphthalein, a solution of which the boiler attendant has always ready at hand. A sample, however, is examined every day in the laboratory, and the mere depth of colour produced by adding phenolphthalein is sufficient to denote if the correct quantity of soda has been used. For two weeks we made a determination daily of the excess of soda by titration with sulphuric acid, using phenolphthalein as indicator, and found per litre 0·046, 0·031, 0·031, 0·138, 0·092, 0·046, 0·183, 0·031, 0·153, 0·198, 0·046,

---

* From the *Zeit. Angew. Chemie*, 1892, p. 15.—Communicated by H. H. B. Shepherd.

0·122 grm. carbonate in excess. These figures are taken from our actual working of the process, and they show that an ordinary boilerman is quite able to master the work required. The boiler was worked day and night uninterruptedly for thirteen weeks, and blown off every day from the highest to the lowest water level. When laid off there was a trifling quantity of sludge in the boiler, and in a part of the tubes a deposit of sulphate of lime of about the thickness of a sheet of paper; this, however, was easily scraped off. The following analyses by Dr. Farnsteiner show the composition of the water used:—

| | Grms. per 100 litres. | |
|---|---|---|
| | Before Purification. | After Purification. |
| Residue | 32·0 | 37·9 |
| Lime | 4·7 | 1·1 |
| Magnesia | 1·3 | 1·0 |
| Sulphuric acid | 3·5 | 3·5 |
| Silicic acid | 1·1 | 1·1 |
| Sodium chloride | 16·7 | 16·1 |
| ,, carbonate | — | 13·8 |
| Combined carbonic acid | 3·3 | — |
| | 30·6 | 36·6 |

My own analysis of the water taken from the boiler at the end of the thirteen weeks was as follows:—

| | Grms. per 100 litres. |
|---|---|
| Residue | 751·7 |
| Silicic acid | 0·7 |
| Magnesium sulphate | 2·5 |
| Calcium sulphate | 17·3 |
| Sodium sulphate | 107·2 |
| ,, carbonate | 12·2 |
| ,, chloride | 581·6 |
| Oxide of iron | 1·8 |
| | 723·3 |

The analysis of the sludge was as follows:—

| | |
|---|---|
| Insoluble matter | 10·00 |
| Calcium carbonate | 55·86 |
| ,, sulphate | 4·87 |
| Magnesia hydrate | 21·74 |
| Oxide of iron | 7·53 |
| | 100·00 |

The sludge gave only a dark green colour with potassium ferricyanide.

The result does not at the first glance seem very satisfactory, since only three-fourths of the lime and practically none of the magnesia was precipitated. If, however, we consider the ultimate result—the analysis of the water remaining in the boiler at the end of the period and the interior condition of the boiler—we see how the excess of soda by concentration has caused the almost complete separation of the salts which cause incrustation.

We have now to consider the effect of supplementing the carbonate of soda either by caustic soda, as used by Dehne, or by quicklime as used by Dervaux. As neither, however, effects a more complete precipitation of the lime than carbonate of soda does alone, they offer no advantage from the point of view of hindering the formation of sulphate of lime deposits. It is true a more complete separation of magnesia is possible by their use, but this in our case is superfluous, since carbonate of soda alone is sufficient to keep the magnesia within bounds.

Dehne makes it a special point that water treated by his method will indicate 0° of hardness. A chemist working in his laboratory can, of course, remove everything capable of being precipitated without using an appreciable excess of reagents; an ordinary boilerman, however, could scarcely accomplish this feat, and to attempt to compile from the results of a single analysis a code of directions once for all, is, from a chemist's point of view, inadmissible. Dehne's system also (at any rate as far as the chemical part of it is concerned), necessitates a knowledge of the "negative hardness" of the water, *i.e.*, the percentage of magnesia. This is needful in order to insure the removal of the excess of caustic soda, without which the promised results are not obtainable. Many instances could be given of the evil effect of such an excess. For example, the board of management of the local quay (Hamburg), finding the river water too impure for their boiler, sank a well to obtain another supply. This well-water, however, proved to be variable in composition, and not at all suitable for the purpose. A sample was found by Wibel to contain per 100,000 parts:—

| | |
|---|---|
| Calcium carbonate | 23·2 |
| Calcium sulphate | 60·0 |
| Magnesium sulphate | 18·0 |

The water was purified by Dehne's method with a mixture of caustic and carbonate of soda with the result that after a short time the boiler became useless. According to the official report, the use of too large a quantity of caustic soda had caused its ruin. A deeper well now supplies an excellent water, free from gypsum, and containing 14·1 parts calcium carbonate and 1·6 parts magnesium carbonate per 100,000, and Dehne's system is given up.

An analogous case is reported by Münter, of Halle. This likewise concerns newly erected boilers fed with water purified by caustic and carbonate of soda. The boiler plates became corroded, and an analysis of the water revealed the presence of sulphate of soda and sufficient oxide of iron to colour the water red. A somewhat similar experience is reported by Abel, of Frankfurt.

This all tends to show the undesirability of regarding the subject of water purification as an engineer's question only, and indicates that its importance is sufficient to demand a greater influence on the part of the chemist. The services rendered by our boiler inspection societies with their staffs of engineers are certainly, as far as they go, admirable, but with chemical questions they are less competent to deal, and if owners of works had the advantage of a chemical as well as a technical adviser always at hand, such frauds as those of the anti-incrustator nostrums could not be carried to such a pitch.

Two important advantages are gained by the use of carbonate of soda alone, which are lost if caustic soda (or what, chemically speaking, is the same thing, caustic lime and carbonate of soda) be substituted:—

1. The easy control over the use of the reagents, and consequent avoidance of either too large or too small a quantity.
2. The knowledge that some excess, if not of unusual proportions, does no harm.

The advantage gained by the use of caustic soda in exchange for the above is, as has already been shown, a pure illusion.

Were it possible, however, to reach Dehne's ideal, and to obtain a water showing 0° hardness and no negative hardness, it would still be undesirable to do so; for, according to Burgdoff, unless *some* sludge is deposited in a boiler it does not remain tight.

For the rest it is quite easy to assure one's self that the excess of carbonate of soda in the boiler water is not too large. All that is necessary is to draw off a little water from time to time, and notice if it gives a large precipitate with a solution of calcium sulphate,—a test any boilerman is capable of making; or phenolphthalein may be used, in which case the indication is conveyed by the colour imparted to the water.

Langfurth recommends, as a preventive against boiler incrustation without the use of chemicals, the plan o blowing off the water as soon as the concentration has reached the point at which gypsum begins to separate out,—a plan which has been used successfully with locomotive boilers.

An indirect means of diminishing the formation of incrustation consists in condensing the exhaust steam and using it for feed water, and apparatus have been constructed for this purpose by Klein, Schanzlin, and Becker. The plan can be recommended in cases where the lubricating oils are exclusively mineral; with animal or vegetable oils, however, it is open to very grave suspicion, as fatty acids are sure to be formed in the boiler, which not only of themselves cause corrosion, but form combinations with the lime and magnesia salts, giving rise to incrustation of a very malignant description.

In conclusion, a few words concerning the many bogus anti-incrustator compounds, which are continually being pressed upon the public under most seductive appellations. A determined crusade, not altogether destitute of results, was fought against them by the Heiz experimental station in Karlsruhe. These nostrums have but one action in common which can be relied upon: they fill the pockets of the vendors so long as fools are forthcoming to be victimised. In other respects they are mostly either useless or else positively harmful, whilst the few that are really compounded with a view to efficiency are offered at three or four times their actual value, sometimes even more.

## A METHOD FOR DETERMINING THALLIUM BY TITRATION.

By K. SPONHOLZ.

In a neutral or acid solution a thallous salt may be converted by bromine-water into a corresponding thallic salt. The oxidation is instantaneous, and as its end is shown with sufficient precision by the liquid turning yellow, this reaction may be used for the quantitative determination of thallium. Two atoms of bromine correspond to one atom of thallium. For instance, for 0·2176 grm. $TlNO_3$ = 0·1669 grm. Tl there were used 10·5 c.c. bromine water, containing per c.c. 0·01244 grm. bromine. Consequently, 0·0008175 atom Tl represents 0·001635 atom bromine, or 1 atom Tl = 2 atoms bromine.

| Thallium weighed (as $TlNO_3$). | | Thallium found. |
|---|---|---|
| 0·4894 grm. | .. .. .. .. | Mean 0·4890 |
| 0·1669 ,, | .. .. .. .. | ,, 0·1666 |
| 0·0166 ,, | .. .. .. .. | ,, 0·0159 |

For effecting the titration we prepare a 1-6th normal bromine-water (for determining larger quantities a more concentrated solution may be used) by means of potassium iodide and sodium thiosulphate. The point of a burette, graduated in 1-10th c.c., is plunged into the acid solution of thallium, and the bromine is allowed to flow in until the excess of bromine causes a distinct yellowness of the thallium solution to appear. The immersion of the point of the burette is necessary, as otherwise the determination is rendered inaccurate by the evaporation of the bromine. The liquid must also be acidified, as thallic salts are decomposed by water, and after the separation of the dark coloured thallium hydroxide the end of the reaction cannot be distinctly recognised. As a correction, the quantity of bromine is determined which gives a distinct yellow colour to a volume of water equal to the thallium solution. It is trifling, but it occasions slight deviations from the mean values.

The standard of the bromine solution must be re-determined each time when the burette is filled, which may be effected expeditiously by means of the method with potassium iodide and sodium thiosulphate. In consequence of the rapid evaporation of the bromine, the titration must be effected at once, and it is well to use only the first 30 to 35 c.c. of a burette holding 50 c.c. Or the standard may be determined both before and after the titration.—*Zeit. Anal. Chemie.*

## PHYSICAL PROPERTIES OF MELTED RUTHENIUM.

By A. JOLY.

Of the six metals forming the platinum group there are three (platinum, iridium, and palladium) the physical properties of which have been more particularly examined by H. Sainte-Claire Deville and Debray. I purpose completing the study of the metals of the groups as regards the three rarer metals, rhodium, osmium, and ruthenium.

This study has become possible for ruthenium in particular, of which I have prepared 3 kilos. in a state of purity. Further, thanks to the inexhaustible kindness of Mr. G. Matthey, I am at present operating on some 50 kilos. of residues from the preparation of iridium, which will enable me to obtain by a new method 10 kilos. of this rare metal. In order to bring the metal into a state comparable to that of the other platinum metals, I intend melting it in a large mass.

Ruthenium is, along with osmium, the most refractory of the platinum metals. Deville and Debray have only with much difficulty succeeded in melting some small globules with the oxyhydrogen blowpipe. During this operation we are incommoded by the oxidisability of the metal, which tends to be transformed into the volatile oxide $RuO_4$. It was evident *à priori* that one might easily succeed with the electric arc. With the electric installation at my disposal, I was able to fuse small globules of from 1 to 2 grms. The particles thus obtained have been melted into reguli of from 25 to 30 grms.—thanks to the kindness of M. de Nerville, who placed a more powerful arc at my disposal.

By means of raising the metal suddenly to a temperature much above its melting-point, the fusion is effected in a few moments, and the loss by volatilisation is scarcely sensible. We scarcely perceive the characteristic odour of the peroxide, but whilst cooling it becomes covered with the blue bioxide. After remaining for a few moments in aqua regia, which attacks neither the metal nor the oxide, then in hydrofluoric acid, and a final reduction in hydrogen, the metal is laid bare. By its grey colour it approximates to iron rather than platinum. Its structure is crystalline, and hence it is brittle in the cold. If heated to redness in the flame of the oxyhydrogen blowpipe it may be flattened out and then breaks. Further, the metal spirts strongly at the moment of solidification, and the globules are almost always full of cavities.

The specific gravity of the metal melted and pulverised is at 0°, and referred to water at 4° = 12·063, the metal being the same which had served for the determination of the atomic weight (*Comptes Rendus*, cviii., 946). For the same sample not fused M. Violle found the specific gravity 12·002. In same apparatus and under the same conditions of temperature, the fusion of ruthenium is more difficult than that of rhodium, which, in turn, is melted with rather more difficulty than platinum; it is remarkably harder to melt than iridium (1950°).

As for the exact melting-point, M. Violle, whose beautiful researches on the measurement of high temperatures are well known, has undertaken its determination. In the conditions at which ruthenium melts, osmium is merely agglomerated and fritted. Iridium osmide, which cannot be melted with the oxyhydrogen blowpipe, is melted with great difficulty into a white crystalline mass, which the best tempered tools do not succeed in cutting.—*Comptes Rendus*, cxvi., p. 430.

## DETERMINATION OF FLUORINE IN COMBUSTIBLE GASES.

By MAURICE MESLANS.

Organic fluorides are in general very stable; the hydrofluoric ethers especially are decomposed only under the action of an elevated temperature, and when the compounds are gaseous the determination of the fluorine presents some difficulties.

The following method appears to furnish at once the most accurate and expeditious results:—

When the combustible organic fluorides are burnt in oxygen, the fluorine is entirely transformed into hydrofluoric acid if the molecule contains the quantity of hydrogen necessary for this transformation. We may then either perform a volumetric determination of this acid by means of an alkaline solution, or convert it into calcium fluoride and thus weigh the fluorine.

In each case the apparatus is composed of a glass combustion-flask, holding about 500 c.c., and closed with a caoutchouc stopper pierced with three holes. One of these gives passage to a glass cock, in which is cemented a tube of platinum, descending to the centre of the flask. The two others give passage to two glass tubes, in which two thick platinum tubes are cemented. Within the flask one of the wires is in contact with the platinum tube, the other descends parallel to it. A finer platinum wire is coiled round the platinum tube, and its spirals are continued in the direction of its prolongation, forming thus an open tube, the extremity of which is fixed upon the second conductor. The spiral can be raised to incandescence by means of an electric current.

*Volumetric Determination.*—We place in the flask a known volume of a dilute standard solution of potassa, we form a vacuum in it by means of a water air-pump, and we introduce about 400 c.c. of oxygen; a partial vacuum (about 10 c.m. of mercury) is preserved in the flask.

The gas to be analysed is measured over mercury into a bell graduated and fitted with a cock; a caoutchouc tube connects the bell to the flask. By manipulating the cocks, the gas is caused to pass slowly from the bell into the flask. As it issues from the platinum tube it meets the incandescent spiral and is at once ignited. Whilst holding the tube in the hand with its neck almost horizontal, we give it a movement which turns the liquid to the interior and causes it continually to moisten the sides; the hydrofluoric acid formed by the combustion is immediately absorbed by the alkaline liquid and the glass is not attacked. When the bell is filled with mercury we close the cock for a moment, and after having introduced a few c.c. of air we open the cock again to drive into the flask the gas contained in the tube. It is then merely necessary to titrate the liquid in order to find the weight of the hydrofluoric acid absorbed.

*Determination in the State of Calcium Fluoride.*—To determine the fluorine by weight we operate in the same manner, but substitute for the standard alkaline liquid a pure milk of lime. After the combustion, the flask contains a mixture of lime and of calcium carbonate and fluoride. This mixture is poured into a platinum capsule in which we collect the washing-waters; after evaporation on the water-bath we ignite to render the calcium fluoride easy to filter. It is re-dissolved in acetic acid and evaporated to dryness on the water-bath. After having exhausted the residue with boiling water, we filter, ignite, and weigh the calcium fluoride.

If we wish to operate upon a very large volume of gas we may do it without increasing the bulk of the combustion-flask. It is sufficient to substitute for the simple cock a 3-way cock connected by its third branch with a receiver of oxygen. The products of combustion being entirely absorbed by the reagent, a vacuum is produced in the flask by the combustion itself, and to continue the operation it is merely necessary to introduce a new charge of oxygen.—*Bull. Soc. Chim. de Paris*, vols. ix.—x, No. 4, p. 109.

## THE PHOTOGRAPHIC PROPERTIES OF THE CERIUM SALTS.

By MM. AUGUSTE and LOUIS LUMIÈRE.

We know that cerium yields two principal series of salts. The former are very stable, whilst the ceric salts are brought back to the lower stage of oxidation even by feeble reducing agents. Some among them, more especially the organic salts, are even reduced spontaneously as soon as formed, so that hitherto it has not been found possible to isolate them.

The easy reducibility of the ceric salts has led us to study the action of light upon these substances, and we have been able to observe that this action effects a rapid reduction which may serve as a basis for the establishment of interesting photographic procedures.

Among the mineral salts which have yielded us the best results we may mention ceric sulphate and nitrrate obtained by dissolving ceric hydroxide in sulphuric or nitric acids. The aqueous solutions of these salts have served to saturate sheets of paper, suitably sized and coated with a thin layer of gelatin, which the cerium salt colours an intense yellow. After drying in the dark, the papers were exposed to light under a positive proof. In all the transparent parts the luminous rays reduce the ceric salt to the cerous state, and the paper is decolorised at these parts. This progressive decolouration enables us to follow the action of the light and to stop the impression at the proper moment.

The proof when thus obtained must be treated with a reagent capable of differentiating the cerous from the ceric salt, so as to accentuate and fix the image. In an analogous process with the manganic salts, which we have formerly published (*Bulletin de la Soc. Française de Photographie*, p. 218, 1892), we used the striking oxidising properties of the manganic salts to form insoluble colouring matters with a great number of substances of the aromatic series. In the same manner, if we treat the proofs with cerium salts with these reagents we form and fix colouring matters at the points where the ceric salt has not been reduced by the light. It then suffices to eliminate, by washing, the excess of the reagent as well as the cerous salt to obtain a proof distinctly fixed. It is important that the colouring substance produced should be insoluble, so that it may not be carried away by the washing.

We found, on considering their photographic utilisation, and on comparing the action of the ferric, cobaltic, manganic, and ceric salts upon a great number of substances of the aromatic series, that the ceric salts are capable of yielding coloured reactions much more numerous than the salts of the other metals.

Among the most characteristic reactions we may mention the following:—

In an acid solution the proofs are grey with phenol, green with aniline salts, blue with naphthylamine $\alpha$, brown with amido-benzoic acid, red with parasulphanilic acid, green with the salts of orthotoluidine, &c. On treatment with ammonia the colour changes; it becomes, for instance, violet with aniline, red with methylamine, &c.

Photographic papers prepared with cerium salts possess a much greater sensitiveness than that of the preparations with ferric or manganic salts.—*Comptes Rendus*, cxvi., p. 574.

**Detection of Ammonia with the Nessler Test.**—L. L. de Koninck.—In ammoniacal solutions the Nessler test does not produce the usual yellowish-brown precipitate in presence of alcohol, nor even a colouration. The reaction of ammonia with mercuric chloride (Bohlig's test) is not prevented by alcohol.—*Zeitschrift Analytische Chemie*, Part 2, 1893.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, March 16th, 1893.*

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. Edgar E. Horvill and Edward Brooke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ralph Edward Brown, Perranporth, Truro, Cornwall; William Robert Burnett, Wiesbaden, Rollupitiga Road, Colombo, Ceylon; Joshua Buchanan, 63, West Cumberland Street, Glasgow; Robert Cecil T. Evans, Swan's Nest, Stratford-on-Avon; Sorabji Manekji Kaka, M.R.C.S., Karachi, Sind, India; Raffaello Nasini, Padua; John Wilkinson, Gas Works, Drighlington, Yorks.

Of the following papers those marked * were read:—

*131. "*The Limits of Accuracy of Gold Bullion Assaying, and the Losses of Gold Incidental to it.*" By T. K. ROSE.

Some of the causes of the errors in the assay of gold bullion by the ordinary method are referred to, and it is shown that—

1. A higher degree of accuracy is attained if the weighings be made with the precautions recommended by Kohlrausch and others on a balance indicating differences of 0·01 per 1000 (½ grm.), instead of 0·05 per 1000, which is the smallest difference shown on ordinary assay balances.

2. Differences either in the amount of copper present to the extent of only 16 parts per 1000 of alloy, or in the amount of silver added to the extent of 3 per cent, produce alterations in the "surcharge" of about 0·05 and 0·1 per 1000 respectively, the "surcharge" being the difference in weight between the gold existent in the assay piece originally taken and the cornet finally obtained; it is the algebraical sum of the gold lost and the silver remaining undissolved by the acids. The reduction in the surcharge due to the presence of antimony, zinc, tellurium, iron, or nickel is also given.

It therefore follows that, in order to ensure accuracy, check assays must be made on alloys of the same composition as those under examination.

3. The want of uniformity of temperature ordinarily prevailing in the muffle furnace during cupellation causes variations in the surcharge. The temperatures of the different parts of a muffle at the Royal Mint were taken during cupellation by a thermoelectric pyrometer—consisting of a platinum and rhodioplatinum couple—on three occasions, from which it appears that the mean temperature of the muffle was 1063·7°. At this temperature a rise of about 5° is found to be accompanied by a reduction in the surcharge of about 0·01 per 1000.

If attention be paid to these points, the gold in bullion of a high degree of purity can be determined within a range of ±0·02 per 1000, the limits of accuracy having been previously considered to be ±0·10 per 1000. This extreme degree of accuracy is only possible if the check gold be pure.

In the second part of the paper the losses of gold in bullion assaying are estimated. They are due to (1) absorption by the cupel; (2) volatilisation in the muffle; (3) dissolution in the parting acid.

The results of a number of assays are given, the gold having been in each case recovered from the cupels and acids, and, after the gold so recovered has been allowed for, the loss by volatilisation is estimated by difference. The losses, in parts per 1000, observed in the assay of standard gold (916·6 fine) were as in accompanying Table.

| | A. | B. | C. |
|---|---|---|---|
| In cupel .. .. .. | 0·513 | 0·36 | 0·51 |
| ,, first acid .. .. | ? | 0·01 | 0·03 |
| ,, second acid .. | 0·012 | 0·02 | 0·04 |
| Volatilised .. .. | 0·075 | 0·05 | 0·06 |
| Total loss .. | 0·600 | 0·44 | 0·64 |

A and B are means of four, and C a mean of three, determinations. Other results are also given.

The determination of the amount of gold volatilised is only approximate, as the result obtained represents the algebraical sum of the errors in several estimations added to the true amount. However, it probably usually lies between 0·5 and 0·1 per 1000.

*132. "*The Volatilisation of Gold.*" By T. K. ROSE.

The loss of gold involved in the fusion of the pure metal and its alloys was investigated by subjecting small test pieces of from 0·5 to 2 grms. in weight to a high temperature under varying conditions on bone-ash cupels placed in a muffle. The work may be considered to be a continuation of the researches of James Napier (*J. Chem. Soc.*, x., 229; xi., 171). The temperatures varied from 1045° to 1300°, and were measured by either a platinum and rhodioplatinum couple or the optical pyrometer devised by M. le Chatelier. The losses of gold could not be measured by the alteration of the mass of the test pieces in the muffle owing to absorption of gases, which sensibly augment the weight of the gold buttons. The true loss was found by assaying the buttons after fusion.

A considerable number of results are quoted. The chief points of interest to which attention is drawn are that:—

1. An increase in the loss of gold takes place when the temperature is high, pure gold losing four times as much at 1245° as at 1090°.

2. A large amount of gold is volatilised in an atmosphere mainly consisting of carbonic oxide, while a small amount is lost in coal gas.

3. A comparatively small amount of gold is carried away by the more volatile metals, copper appearing to exert an exceptional action; metals which are easily volatilised do not appear to be completely driven off by the highest temperatures attained in the experiments.

4. A large proportion of gold is lost in the case of alloys which form flat buttons on the cupel, and, conversely, a small proportion is lost from spherical ones, although the surface actually exposed is greater in the latter case than in the former. A current of air or gas passing over the buttons does not seem to increase the loss, provided the surface of the molten metal remain at rest. These results point to the conclusion that the conditions which lower the surface tension of the gold button simultaneously raise the vapour pressure of the gold.

### DISCUSSION.

Professor ROBERTS-AUSTEN said that, prior to the last few weeks, he should certainly have considered that the accuracy of an assay of gold was comprised within a range of ±2/10,000. Mr. Rose had, however, tracked the errors to their respective sources, and had shown that a still higher degree of accuracy can be attained in ordinary work. It was not a little remarkable that although Princep (one of the best Assay Masters who ever held that important office) had clearly indicated in 1827 the importance of knowing the variations of temperature in an assay muffle, no one had attacked the problem until Mr. Rose took it in hand. Although questions connected with assaying did not often come before the Society, they were matters to which the fathers of chemistry had given much attention. He might remind the Society that, apart from their scientific interest, these minute questions connected with assaying assumed considerable industrial importance. During his connection with the Mint, extending over more than twenty years, he had been responsible for the standard pureness of more than 600 tons of gold, the value of which was over 80 millions sterling. As regards the number of assays made, he and his two colleagues, the Assistant Assayers, had made in the past year no fewer than 30,000 assays of gold, and they had every reason to believe that their average accuracy was 1·10,000th part.

*133. "*Note on the Boiling-point of Nitrous Oxide at Atmospheric Pressure, and on the Melting-point of Solid Nitrous Oxide.*" By William Ramsay, F.R.S., and John Shields, Ph.D., B.Sc.

The boiling-point of the liquid nitrous oxide was found by means of a constant volume thermometer filled with hydrogen to be −89·8°; and the melting-point of the solid to be −102·3°. The method adopted is one in which the errors due to the gas in the stem of the thermometer not being at the same temperature as that in the bulb and to the alteration of the capacity of the bulb by change of temperature are eliminated.

*134. "*The Isomerism of the Paraffinic Aldoximes.*" By Wyndham R. Dunstan and T. S. Dymond.

Several attempts have been made during recent years to obtain evidence of an isomerism in the series of paraffinic aldoximes similar to that which has been observed and studied in a number of the corresponding benzenoid derivatives. These attempts have so far been unsuccessful, and, in fact, it has been concluded from the recent experiments of Dollfus (*Ber.*, 1892, 1908) that paraffinic aldoximes exist only in one form. The fact that the paraffinic aldoximes were, until recently, known only in the liquid condition has, however, made such enquiries difficult if not inconclusive. The problem has assumed a new aspect since the authors' discovery that acetaldoxime could be crystallised, and that when heated for some time above their melting-point (m p. 46·5°) the crystals gradually undergo isomeric change into a modification which is liquid at the ordinary temperature, but which, on cooling, slowly changes back again into the crystalline form. The physical differences between the two isomerides are for the most part very slight, there being but small differences in their relative densities and magnetic rotations. Further experiments have been made in order to compare these two modifications with the two isomeric benzaldoximes discovered by Beckmann, and, if possible, to determine the nature of the isomerism. Chemical experiments with the two modifications of acetaldoxime are difficult to carry out, owing to their instability and especially to the circumstance that the liquid modification cannot be obtained free from its someride.

When acted on by acetic anhydride neither modification furnishes any appreciable quantity of acetonitrile, except at temperatures near 100°. By working under conditions whereby the occurrence of isomeric change is minimised, the crystalline acetaldoxime is converted by acetic anhydride into a liquid acetyl derivative which is so unstable that it cannot be isolated in the pure state; it decomposes when distilled, even under reduced pressure. It is hydrolysed by water as well as by dilute alkalis, yielding acetic acid and the aldoxime. The liquid acetaldoxime also furnishes an acetyl derivative, which apparently is identical with that obtained from the crystalline isomeride. In some cases the action of acetic anhydride on both modifications has led to the production of a small quantity of *hydroxyacetylaldoxime* (*diacethydroxamic acid*), $CH_3C(OH)NO(COCH_3)$, a solid crystalline substance melting at 87·5°.

Both modifications of acetaldoxime are converted by hydrogen chloride into the same crystalline hydrochloride ($CH_3CH:N\cdot OH,HCl$), a very hygroscopic substance.

By the action of phosphoric chloride at a low temperature on an ethereal solution of the crystalline acetaldoxime a product is obtained which on hydrolysis gives ammonia and acetic acid as well as methylamine and formic acid. A determination of the quantity that is formed of each of these substances has shown that 90 per cent of the aldoxime is converted into ammonia and acetic acid, and the remainder into methylamine and formic acid. When acted on by phosphoric chloride at a higher temperature, the liquid acetaldoxime is converted into a product which on hydrolysis furnishes the same products as the crystalline modification, and in almost the same proportion.

On the other hand, the two isomerides afford only ammonia and acetic acid when acted on by phosphorous chloride.

*Propionaldoxime*, $C_2H_5\cdot CH:NOH$, has hitherto been known only as a liquid (b. p. 132°); it may, however, be crystallised by cooling it to about −12°, and thoroughly stirring the liquid. The crystals closely resemble those of acetaldoxime in appearance; they melt at 22°, that is, 24·5° lower than the acetic compound. If it be melted and the resulting liquid be heated for some time, propionaldoxime gradually undergoes an isomeric change similar to that suffered by acetaldoxime, being converted into a liquid which cannot be made to crystallise by any means unless it be cooled below −10°, when crystals of the other modification separate, and by degrees entire reconversion into this form takes place.

There is only a slight difference in the relative densities of the two modifications. Phosphoric chloride acts on a well-cooled ethereal solution of the crystalline propionaldoxime, and when the mixture is poured into water ammonia and propionic acid are produced as well as ethylamine and formic acid. About 94 per cent of the aldoxime is converted into ammonia and propionic acid, and about 6 per cent into ethylamine and formic acid.

When acted on by phosphorous chloride, however, it affords only ammonia and propionic acid.

*Isobutyric aldoxime* is a liquid (b. p. 139·5°) which does not crystallise even when cooled to −80°. When acted on by phosphoric chloride, about 60 per cent of the aldoxime is converted into ammonia and isobutyric acid, and about 40 per cent into isopropylamine and formic acid.

It would appear from these results that further study is requisite to establish criteria of stereochemical isomerism in the case of these oximes. It would seem that the action of phosphoric chloride in particular is attended with structural isomeric change, and that the production by Beckmann's method of two acids and two amines cannot be regarded as evidence of the existence in the compound of two stereochemical forms of the original oxime, as has been suggested by Hantzsch, in the case of certain ketoximes.

It has, therefore, been determined to submit the two isomeric benzaldoximes to a more minute examination than they have hitherto received; these aldoximes being selected, rather than any of the paraffinoid compounds, on account of their greater stability. Progress has already been made with this work.

135. "*The Mineral Waters of Askern, in Yorkshire.*" By C. H. Bothamley.

Although the mineral waters of Askern have a well-established reputation in the treatment of chronic rheumatism and of skin diseases, no analyses of them have been made since those of Lankester and West in or about the year 1840.

There are at present four wells or springs in the peat common, on the edge of which the village of Askern stands, and to each of these is attached a pump room and a suite of baths. The author has examined samples of the waters collected at intervals extending over a period of nearly two years. They are surface or shallow spring waters, and are mainly solutions of calcium and magnesium carbonates and sulphates, containing a large quantity of dissolved peaty matter and a considerable amount of hydrogen sulphide; minute traces of iodine and lithium, but neither bromine or potassium, were detected. The approximate composition of the four waters, in grms. per litre, is given in the Table.

It is pointed out that the production of the sulphuretted hydrogen is probably due to the action of an organism, although hitherto the author has failed in isolating one.

| | Mother Close Well. | Terrace Baths. | Charity Baths. | Manor Baths. |
|---|---|---|---|---|
| Calcium carbonate .. | 0·8417 | 0·8232 | 0·6825 | 0·6698 |
| „ silicate.. .. | 0·0281 | 0·0262 | 0·0443 | 0·0449 |
| „ sulphate .. | 0·5222 | 0·4434 | 0·4938 | 0·5151 |
| Magnesium sulphate.. | 0·3874 | 0·4288 | 0·7184 | 0·6834 |
| Sodium chloride . .. | 0·0346 | 0·0989 | 0·1190 | 0·1205 |
| „ sulphate . .. | 0·0426 | 0·0220 | 0·0659 | 0·0599 |
| Total .. .. .. | 1·8566 | 1·8425 | 2·1239 | 2·0936 |
| Hydrogen sulphide .. | 56·7 c.c. | 49·5 c.c. | 34·8 c.c. | 37·3 c.c. |

136. "*Note on the Distribution of Acidic and Alkalinic Radicles in a Solution containing Calcium, Magnesium, Carbonates, and Sulphates; and on the Composition of Mineral Waters.*" By C. H. Bothamley.

In examining the mineral waters of Askern, it was found that the precipitate formed when the "free" carbon dioxide was expelled was almost pure calcium carbonate, and contained the merest trace of magnesium, although this element was present in considerable quantity. Direct experiments show that an excess of well-washed precipitated magnesium carbonate completely precipitates calcium from a solution of calcium sulphate in the absence of "free" carbon dioxide, and that there is practically no reverse action when a solution of magnesium sulphate is placed in contact with a large excess of precipitated calcium carbonate. When solutions of calcium carbonate and magnesium sulphate are mixed together and the "free" carbon dioxide is expelled by the action of heat or by the passage of a current of hydrogen, the precipitate contains only a mere trace of magnesium. The same result is obtained when a solution of magnesium carbonate is mixed with a solution of calcium sulphate and the "free" carbon dioxide is expelled by a current of hydrogen.

The existing thermochemical data afford no explanation of these results.

The author concludes that if we put aside the question of ionic dissociation in solution, and represent mineral waters and similar solutions of calcium, magnesium, and the carbonic and sulphuric acid radicles as containing salts as such, the sulphuric radicle must be regarded as combining by preference with magnesium and not with calcium, as is generally supposed. In the case of the Askern waters this view is supported by their therapeutic action.

137. "*A Magnesium Compound of Diphenyl.*" By W. R. Hodgkinson.

The energetic manner in which ammonia gas and some ammonium salts are decomposed by magnesium suggested that perhaps benzenoid amines, and especially anilids, might give metallic derivatives. Magnesium, however, is entirely without action on dry aniline, toluidine, and other similar alkaloids; and form- and acetanilid and even phthalanil are unaffected when passed over the metal heated to about 400°.

When phenylhydrazine is warmed with magnesium, either in the form of filings, ribbon, or wire, action begins at about 150°; using filings, if not carefully controlled, the action becomes almost explosive, the temperature attained being frequently sufficient to inflame the products. The products which volatilise during the process are aniline, benzene, ammonia, and nitrogen; a compound containing the metal being left in the retort.

The magnesium compound is a solid, nearly white substance; it does not volatilise, but on heating the contents of the retort in which the operation has been conducted to nearly a red heat, an oil distils over from which a small quantity of diphenyl may be isolated. On admitting air into the retort before it is quite cold, the substance turns brown, and in most instances inflames. Water has a similar effect on the hot substance.

Boiling benzene, and especially cymene, dissolve a metallic compound which is deposited partly on cooling and partly on evaporating off the solvent in a vacuum as a brown amorphous powder; this takes fire on very gently heating it in air, magnesium oxide and much charcoal being left.

As yet the analysis of different preparations of this substance have not been very satisfactory. It certainly does not contain much, if any, nitrogen as an essential element, the highest percentage found being 1¼; this appears to be derived from some nitrogen compound formed by a secondary action and not from a magnesium phenylhydrazine or magnesium aniline.

The unmistakable production of diphenyl on heating the magnesium compound is suggestive of the presence of magnesium diphenyl as one of the products.

The author wishes to reserve the further investigation of the interaction.

138. "*Note on Acetanhydrocitric Acid.* By Felix Klingemann.

The author points out that the acetylanhydrocitric acid described by Easterfield and Sell (*Trans.*, 1892, 1003) had been previously prepared and studied by himself (*Berichte*, 1889, 983); he adversely criticises several of their statements, and quotes analyses of the silver salts of citrodianilic and citro-*p*-toluidic acids, proving that both are mon-acids.

139. "*The Dissolution of Gold in a Solution of Potassium Cyanide.*" By R. C. Maclaurin, B.Sc.

The study of the conditions contributory to the dissolution of gold in solutions of potassium cyanide is become of importance, owing to the recent use of this agent in extracting gold from poor ores. The nature of the changes is disputed; Elsner originally expressed the interaction by the equation—

$$4Au+8KCN+O_2+2OH_2=4AuCN\cdot KCN+4KOH,$$

but McArthur, in a recent paper, has called in question the necessity of oxygen being present. It is a remarkable fact in connection with the process that the rate of dissolution of the gold decreases as the concentration of the cyanide solution increases.

It is shown that dissolution of the metal is conditioned by oxygen, and that the amounts of oxygen absorbed and of gold dissolved are in the ratio O : 2Au. Furthermore, it is shown that the rate of dissolution varies with the strength of the solution, and that it passes through a maximum in passing from dilute to concentrated solution; this variation is traced to a decrease in solubility of oxygen in solutions of potassium cyanide as the concentration increases.

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*Annual General Meeting, March 27th, 1893.*

Prof. A. Crum Brown, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The numerical position of the Society is as follows:—

| | | |
|---|---|---|
| Number of Fellows, March, 1892 .. .. .. | | 1825 |
| Since elected who have paid admission fees .. | | 128 |
| | | 1953 |
| Removed on account of non-payment of subscriptions .. .. .. .. .. .. .. .. .. | 20 | |
| Withdrawn .. .. .. .. .. .. .. .. .. | 18 | |
| Deceased .. .. .. .. .. .. .. .. .. | 20 | |
| | | 58 |
| Present number of Fellows . .. .. .. .. | | 1895 |
| Foreign Members (1892) .. .. .. .. .. | 30 | |
| Since elected.. .. .. .. .. .. .. .. .. | 5 | |
| Present number of Foreign Members .. .. | | 35 |

Twenty Fellows have died within the year:—G. S. Bowler, H. N. Draper, John Hooker, A. W. von Hofmann,

F. C. Hills, W. E. Ivey, Hodgson Jones, Dr. G. D. Longstaff, W. H. Michael, G. H. Makins, J. S. Merry, Dr. T. H. Rowney, John S. Sieber, Professor C. Schorlemmer, A. Norman Tate, Thomas Taylor, Dr. Thos. Walton, J. Septibo Ward, Dr. J. Forbes Watson, Mattieu Williams.

Eighteen Fellows have withdrawn :—Thomas Akitt, Dr. James Bell, Edward Dillon, J. V. Elsden, J. C. Husband, W. E. Halse, Farmer Hall, E. T. Kensington, Lawrence Levy, Chas. O'Neill, Dr. G. S. W. Ogg, Magnus Ohren, G. A. Parkinson, H. F. Pasley, Edward Purser, A. H. Tapp, E. W. Wiltshire, Dr. George Wilson.

The names of twenty Fellows have been removed from the Register :—James Anderson, Dr. J. B. Battershall, Frank Calder, G. E. R. Ellis, D. R. S. Galbraith, G. W. S. Howson, J. J. Hickey, A. C. M. Ingram, George Lloyd, H. Oliver Mintz, J. W. O'Connor, C. T. Rhodes, E. Reckett, W. Symons, H. L. Schubert, H. L. Sulman, Stanley Southam, T. B. Tyson, Dr. F. W. Traphagen, M. Whitley Williams.

Professors Emil Fischer, Carl Graebe, Adolph Liben, Hugo Schiff, and Th. Schloesing have been elected Foreign Members.

No fewer than 139 communications are recorded in the *Proceedings*, this being the largest number yet contributed to the Society in a single session.

The 1892 volume of the *Transactions* contains ninety papers, occupying 1096 pages, while the Abstracts occupy 1536 pages.

From the commencement of this year, the Abstracts have been so paged that it will be possible to bind them in two sections, the one section to include all papers on organic chemistry, the other the remaining branches; this arrangement has been adopted by the Council in the belief that it will tend to promote continuity and facilitate reference.

. The Council have resolved that a subject index of the original communications published in the Society's Journal during the years 1873—1892 inclusive shall be published. It is suggested that this shall be a true index and not a mere recital of titles; the precise form it shall take is, therefore, under consideration.

Two "Memorial Lectures" have been delivered during the year, commemorating the work of two deceased Foreign Members, Hermann Kopp and Jean Servais Stas: that on Stas was prepared by Professor Mallet, and that on Kopp by the Treasurer, Professor Thorpe; the Society and chemists generally will undoubtedly feel that they are much indebted to both of these two gentlemen when the two memoirs are placed in their hands. In the first of these lectures, Professor Mallet, besides referring to Stas's work, has carefully considered its bearings and has indicated directions in which enquiries may, with advantage, be now carried on; the example that he has set will undoubtedly be of great service in the preparation of similar memoirs. The Council have resolved to print an extra number of copies of such lectures, and when in possession of a sufficient number to form a volume, to issue them in a separate form.

Among the Fellows deceased during the year there are two whose services to the Society have been of an *altogether* special character—Professor von Hofmann and Dr. G. B. Longstaff; special resolutions of condolence have been passed by the Council and communicated to their families. Von Hofmann's work will be considered in the coming Hofmann Memorial Lecture. In Dr. Longstaff the Society loses one of its original Fellows, of whom now very few remain. He was a very active member of the Society in early days, and within recent years his munificence secured the establishment of the Research Fund; owing to his stipulation that a medal should be awarded at least triennially to a Fellow of the Society in recognition of the value of his researches, Dr. Longstaff's name will ever remain associated with the Society and with chemical science, as the Council determined that the medal should be known as the Longstaff Medal.

Towards the close of the year, an address, offering the Society's congratulations on the occasion of the celebration of its twenty-fifth anniversary, was forwarded to the *Ber. Deuts. Chem. Gesell.*

An address from the Society was presented to M. Pasteur on the occasion of his 70th birthday.

Communications were addressed by the Foreign Secretary to the University of Padua on the occasion of the Galileo celebration, and to the Committee in Stockholm, charged with the erection of a memorial to Scheele in response to invitations to the Society to take part in these proceedings.

The Council are indebted to Mr. E. H. Wollaston for the presentation of a valuable proof engraving of a portrait of Wollaston.

Very considerable additions have been made to the library during the year.

The subject of the admission of women as Fellows, which has been several times discussed by the Council, has been again brought under consideration during the year, but without any resolution being arrived at to propose an alteration in the Bye-laws. It appeared to be generally felt that, although there is no objection in principle to the admission of women as Fellows, the case in their favour is not clearly established by any considerable number of applications.

During the long vacation the meeting room was entirely reconstructed, with the result that a very considerable air space has been gained, tending to the better ventilation of the room; additional accommodation both in sitting space and in entrances and exits has also been secured; and provision has been made for the entrance of fresh air into, and for the removal of vitiated air from, the room. The electric light has been substituted for gas in all the rooms. The apartments were redecorated throughout.

The structural alterations were planned and their execution superintended by Mr. Martin L. Saunders, and the alterations and redecoration of the rooms have been carried out by Messrs. Colls and Sons. The installation of the electric lighting was planned by Prof. Ayrton, to whom the Society is under great obligation for the amount of time and thought he has expended on the work. The business of wiring the building and fixing the fittings for the electric light was entrusted to Messrs. Spagnoletti and Crookes, and the brackets, pendants, &c., were supplied by Messrs. Faraday and Sons.

| | £ | s. | d. |
|---|---|---|---|
| The cost of the structural alterations (including architect's fee) have been .. | 1113 | 14 | 10 |
| The electric light installation having cost | 289 | 0 | 6 |
| | £1402 | 15 | 4 |

It is a matter of congratulation to the Society that the Treasurer has been able to pay these large extra expenses, and at the same time to carry forward the necessary working balance, without touching the Society's funded property.

In the latter part of his address the President discusses the history of the phlogistic theory, and its gradual displacement by more modern views.

Dr. ARMSTRONG proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed. In the course of his remarks, he said that during the past two years, for the first time in the history of the Society, the President had been a Fellow from beyond the Border,—a fact of much importance, as proving that they were in no sense a mere metropolitan society, and that they both desired to secure, and were, indeed, successful in securing, the cooperation of British chemists generally. Dr. GLADSTONE seconded the motion, which was carried by acclamation. The PRESIDENT having thanked the meeting,

Mr. HOLLAND CROMPTON, the Senior Auditor, in the absence of the Treasurer abroad, gave an account of the balance sheet duly audited by Mr. Dymond, Dr. Lawson, and himself. Prof. Thomson subsequently contrasted the chief items of expenditure during this and the previous year. The receipts by admission fees and subscriptions had been £3771 11s. 4d. as against £3545 in the previous year; and £424 15s. 3d. had been realised by the sale of the Journal, instead of only £408 7s. 4d. The Journal had cost £2745 7s. 4d. instead of £2798 15s. 10d.; £327 1s. 1d. had been expended on the library; the alterations had been effected at a cost of £1402 15s. 4d.; the total expenditure being £5287 1s.; so that the ordinary expenditure had been £3884 5s. 8d. as against £3989 1s. 6d. in the previous year. Grants amounting to £200 had been made from the Research Fund.

A vote of thanks to the Treasurer was proposed by Dr. Russell, who dwelt with satisfaction on the fact that it had been possible to meet the expenses of the alterations from the surplus income of this and the previous year without touching the Society's funded property. The vote, having been seconded by Prof. Ramsay, was carried by acclamation.

Mr. Crookes proposed and Mr. Pickering seconded a vote of thanks to the Auditors; the motion having been adopted, Mr. Crompton replied.

A vote of thanks to the Officers and Council was then proposed by Mr. J. Newlands and seconded by Mr. Cassal; Prof. Thomson replied.

Dr. J. Voelcker moved and Mr. Spiller seconded a vote of thanks to the Editor, Sub-Editor, Abstractors, and Librarian. Mr Groves and Dr. Thorne replied.

Mr. W. Foster and Mr. Tutton having been appointed Scrutators, a ballot was taken, and the following were declared elected:—

*President*—H. E. Armstrong, Ph.D., F.R.S.

*Vice-Presidents who have filled the office of President*—Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; Dr. A. Crum-Brown, F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Lord Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents*—E. Atkinson, Ph.D.; A. Vernon Harcourt, F.R.S.; C. O'Sullivan, F.R.S.; John Pattinson; William Ramsay, F.R.S.; William A. Tilden, F.R.S.

*Secretaries*—J. Millar Thomson; Wyndham Dunstan, M.A.

*Foreign Secretary*—Raphael Meldola, F.R.S.

*Treasurer*—T. E. Thorpe, D.Sc., F.R.S.

*Ordinary Members of Council*—Norman Collie, Ph.D.; Charles F. Cross; Harold Dixon, F.R.S.; Bernard Dyer, D.Sc.; Lazarus Fletcher, M.A., F.R.S.; R. J. Friswell; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; W. A. Shenstone; John A. Voelcker, Ph.D.; W. P. Wynne, D.Sc.

The following additions to the bye-laws, proposed by the Council, were then submitted to the meeting and carried:—

1. In Bye-Law XI., after the words: "The ordinary Scientific Meetings of the Society shall be held twice in every month, from November to June inclusive, except in the month of January, when the Society shall meet once only," to add the words "and also at Easter, when, if the Council see fit, there shall also be only one meeting in the month."
2. In Bye-Law XIII. to add the following paragraph:— "At all General Meetings of the Society, whether Annual or Extraordinary, no motion of a proposal to alter the bye-laws shall be considered of which due notice has not been given at least 14 days previously, either at an ordinary Scientific Meeting, or through the agency of the *Proceedings*, or by means of a printed notice addressed to all the resident Fellows."

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 13, March 27, 1893.

**Organic Matters Constituting Vegetable-Soil.**—MM. Berthelot and André.—The author gives analyses of different soils of the Agricultural Station of Meudon. Close I. contains—

| | |
|---|---|
| Organic carbon | 19·1 |
| Hydrogen | 1·5 |
| Nitrogen | 1·7 |
| Organic oxygen | 11·9 |
| Total organic matter | 34·2 |

The authors remark that this is the only soil in which the complete determination of all the elements, mineral and organic, has been effected. This soil is said to be nearly saturated with nitrogen, whilst the soil II., equally rich in carbon, remains capable of absorbing free nitrogen. The authors recognise the action of microbia as gradually transforming barren sands into vegetable mould.

**Researches on Samarium.**—Lecoq de Boisbaudran.—This paper will be inserted in full.

**Distillation of Mixtures of Water and Alcohol.**—E. Sorel.—This paper does not admit of useful abstraction.

**General Method for Calculating the Atomic Weights according to Chemical Analysis.**—G. Hinrichs.—The author considers that the researches of an entire century have established the fact that if we take $O = 16$, the atomic weights of almost all the elements border very closely upon whole numbers; for others, such as Cu and Cl, the value is close upon a whole number and a half. "We may affirm that the most precise determinations of the elements are exactly what they ought to be if all the elements had been formed from a single primitive substance."

**Formation of Gallanilide: its Triacetic and Tribenzoylic Derivatives.**—P. Cazeneuve.—Aniline gallate, if heated to from 105°—110° loses $CO_2$, is transformed into gallanilide by the elimination of water. The anilide of gallic acid may be obtained by causing aniline to react upon digallic acid or gallotannic acid.

No. 14.

**Benzenazocyanacetic Ethers and their Analogues.**—A. Haller and E. Brancovici.—The authors have studied in detail the ethyl- and methyl-benzenazocyanacetates, their constitution, accepting them as true azo-derivatives and not as hydrazone. They also interpret the nature of the isomerism of the α- and β-ethers.

**Attempt at the Condensation of the Acetylcyanacetic Ethers with the Phenols.**—A. Held.—It results that the ethylacetylcyanacetate behaves in a different manner according to the nature of the phenol employed. In the case of normal phenol it yields a substitution and transformation-product of malonic ether, the phenol not entering into reaction. In case of resorcine the nitrile function is saponified, and the same product is obtained as by the condensation of acetylacetic ether with resorcine. With methyl-acetylcyanacetate, no appreciable transformations are produced. If dehydrating agents are employed other than sulphuric acid, such as zinc or aluminium chlorides, the result is nil.

**Synthesis of Erythrite.**—G. Griner.—The author has set out from a non-saturated carbide, divinyl or butadiene, and has obtained an (optically) inactive erythrite incapable of being split up. He is now attempting the formation of a racemic erythrite.

**Action of Temperature on the Rotatory Power of Liquids.**—A. Aignan.—If we calculate the effect on the polarimeter produced on a given radiation by a mixture of two active substances of opposite signs, we see easily that this effect may be nil for suitable proportions of the weights of the two bodies mixed. If there be given such a mixture which is thus *inactive by compensation*, its effect is examined at the same temperature upon a radiation different from the former, it is generally found inactive in one or other direction. If the effect produced by this liquid on the original radiation is examined at different temperatures, we may find that the compensation ceases to exist.

## MISCELLANEOUS.

**Technical Education at Cambridge.**—The Cambridge University extension authorities have already announced as part of the programme of their summer meeting, to be held in Cambridge next Autumn, five courses of practical work in science in the University laboratories and museums, the subjects selected being chemistry, electricity, botany, physiology, and geology. As, however, the date of the summer meeting, July 29 to August 26, is too early for many teachers in elementary schools, whose holidays fall during harvest time, arrangements have also been made for two courses in agricultural chemistry, specially adapted to meet the requirements of teachers sent with scholarships by their respective County Councils. Each course will extend from August 25 to September 12 inclusive, and will thus include sixteen working days, on each of which several hours' work in the University laboratory will be provided. One course—conducted by Mr. Fenton, one of the University demonstrators—is intended for students who have done little or no laboratory work, but have acquired a knowledge of theoretical chemistry, and will be similar to the course given last year, and attended by about 120 County Council scholars. The other course—conducted by Mr. R. H. Adie, one of the Cambridge extension lecturers—will be more advanced in character, and will be adapted to students who went through last year's course with credit, or have done similar work elsewhere. Accommodation for 120 students can be provided at these two courses.

## MEETINGS FOR THE WEEK.

Monday, 24th.—Medical, 8.30.
—— Society of Arts, 8. "Some Masters of Ornament," by Lewis Foreman Day. (Cantor Lectures).
Tuesday, 25th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "Symbolism in Ceremonies, Customs, and Art," by John Macdonell, LL.D.
Wednesday, 26th.—Geological, 8.
—— British Astronomical Association, 5.
—— Society of Arts, 8. "The Optical Correction of Photographic Perspective," by H. Van der Weyde.
Thursday, 27th.—Royal, 4.30.
—— Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
—— Society of Arts, 4.30. "Indian Manufactures—their Present State and Prospects," by Sir Juland Danvers.
—— Institute of Electrical Engineers, 8.
Friday, 28th.—Royal Institution, 9. "The Transmission of a Nervous Impulse," by Prof. Francis Gotch, F.R.S.
—— Physical, 5. "Discussion on the Viscosity of Liquids," by Prof. J. Perry, J. Graham, and L. W. Heath. "On Luminous Discharges in Electrodeless Vacuum Tubes," by E. C. Rimington.
Saturday, 29th.—Royal Institution, 3. "Some Applications of Electricity to Chemistry," by James Swinburne, M.Inst.E.E. (The Tyndall Lectures).

THE CHEMICAL NEWS.

Vol. LXVII., No. 1744.

# THE PRESENCE AND ESTIMATION OF GOLD AND SILVER IN ANTIMONY AND IN BISMUTH.*

By ERNEST A. SMITH, Assoc.R.S.M.,
Assistant Instructor in Assaying, Royal School of Mines, London.

Gold and silver are found associated in larger or smaller quantities with most of the ores of antimony and of bismuth. It is therefore interesting to ascertain to what extent, with the modern methods of extraction, these metals are retained in the metallic antimony and bismuth as they come into the market. The usual methods for estimating the gold and silver present in antimony are scorification and methods involving solution, but in the former case, as not less than 500 grains of antimony have to be operated upon, the method cannot be recommended on account of the large quantity of lead necessary to ensure the elimination of the whole of the antimony. Wet methods also are scarcely applicable, owing to the very small percentage of precious metals contained in the mass of metallic antimony operated upon.

The following method was used and gave very satisfactory results :—

500 grains of the sample of metallic antimony crushed to a fine powder were mixed with—

| | |
|---|---|
| Litharge .. .. .. .. | 1000 grains. |
| Potassium nitrate .. .. | 200 ,, |
| Sodium carbonate .. .. | 200 ,, |

and heated in a crucible in a wind furnace at a dull red heat for about fifteen minutes.

When quite tranquil the contents were poured into an ingot mould, and the button of lead, which weighed about 500 grains and was perfectly malleable, was cupelled direct. The resulting gold and silver button was parted in dilute nitric acid in the usual way.

When necessary the slags were cleaned by crushing to a coarse powder, mixing with 500 grains of litharge and 20 grains of charcoal, and fusing under the same conditions as before.

The following results were obtained with various samples of commercial star antimony :—

| No. of sample. | Per ton of 2240 lbs. | | | | | |
|---|---|---|---|---|---|---|
| | Gold. | | | Silver. | | |
| | Ozs. | Dwt. | Grs. | Ozs. | Dwt. | Grs. |
| 1 .. .. | 0 | 19 | 14 | 1 | 15 | 7 |
| 2 .. .. | 1 | 12 | 0 | 0 | 5 | 5 |
| 3 .. .. | 0 | 4 | 14 | 6 | 4 | 19 |
| 4 .. .. | 0 | 1 | 7 | 0 | 17 | 0 |
| 5 .. .. | | trace | | 0 | 9 | 19 |
| 6 .. .. | 0 | 0 | 16 | 0 | 15 | 0 |
| 7 .. .. | 1 | 15 | 7 | 1 | 12 | 16 |
| 8 .. .. | 0 | 13 | 17 | 0 | 8 | 12 |

To estimate the gold and silver in metallic bismuth 500 grains were carefully cupelled, and the buttons of precious metals thus obtained were parted in the usual manner.

The results obtained for bismuth from various sources, recently purchased in London, are as follows :—

| No. o Sample. | | Per ton of 2240 lbs. | | | | | |
|---|---|---|---|---|---|---|---|
| | | Gold. | | | Silver. | | |
| | | Ozs. | Dwt. | Grs. | Ozs. | Dwt. | Grs. |
| 1 .. .. | | 0 | 11 | 18 | 72 | 16 | 22 |
| 2 .. .. | Australian. | 3 | 11 | 21 | 108 | 8 | 10 |
| 3 .. .. | German. | 0 | 1 | 23 | 23 | 16 | 21 |
| 4 .. .. | American. | 0 | 3 | 6·5 | 23 | 0 | 14 |

The bismuth may be extracted from the cupels by rejecting the white portion and crushing the stained portion to a fine powder and fusing at a red heat with the following fluxes :—

| | |
|---|---|
| Powdered cupels.. .. .. | 1000 grains. |
| Fluorspar .. .. .. .. | 800 ,, |
| Soda carbonate .. .. .. | 400 ,, |
| Borax .. .. .. .. .. | 200 ,, |
| Charcoal powder.. .. .. | 45—50 ,, |

From the results of the quantities of gold and silver obtained from the various samples of metallic antimony and bismuth it is somewhat remarkable that more profitable methods have not been introduced for the extraction of the precious metals.

# THE COMBINATION OF OXYGEN WITH HYDROGEN.

By H. N. WARREN, Research Analyst.

A mixture of two volumes of hydrogen with one of oxygen remains inert until a light is presented to the same,—so read our modern handbooks of chemistry. But oxygen, in admixture with hydrogen, becomes closer allied to water on increase of pressure, until a pressure of 180 atmospheres is attained, when combination takes place with fearful violence. The experiments which are thus presented by the author, of which a brief description will suffice, were constructed electrolytically, as may be readily observed to be the simplest and at the same time most efficient mode of dealing with the gases. Small selected glass tubes, into which two platinum wires were sealed, after introducing into each a c.c. of acidulated water and sealing the further extremity, were subjected to the action of an electric current of six volts. The rapid bursting of the first series of tubes, consequent upon the heating of the small quantity of liquid contained therein, at once suggested the cooling of the same by inserting the sealed tube and its contents in a strong glass vessel containing water. A tube thus mounted was next put upon trial; the electric circuit having been established, the experimenters meanwhile withdrawing themselves to a safe distance, carefully timing the effect.

In previous cases of trial the tubes had burst within three minutes, after applying the current, with a slight explosion; but in this case ten minutes had elapsed, and the action continued as energetic as ever. Fifteen and twenty minutes passed, and the action within the minute vessel continued as briskly as ever; exactly twenty-five minutes had elapsed when a vivid flash, succeeded by a violent report, terminated the experiment, shattering the glass vessel and scattering fragments in all directions.

Some force of the explosion may be understood from the fact of the sealed tube being but an inch and a half in length, and containing only one c.c. of water; nevertheless, portions of glass were hurled with sufficient force in the immediate neighbourhood of the explosion so as to penetrate a wooden bench to the depth of half an inch, whilst an assistant some distance from the spot narrowly escaped severe laceration. Various other tubes were afterwards experimented upon, affording similar results, the pressure, as arrived at by a careful average, amounting to 180 atmospheres.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

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* Abstract of a Paper read before the Society of Chemical Industry, Monday, April 10.

## DETECTION OF EXTRACTED TEA.

By W. A. TICHOMIROW.

The author has made an examination of such tea as is used for the falsification of genuine tea. If dry extracted tea is covered with a cold, saturated solution of copper acetate, the blue colour of the liquid remains unchanged for months. With dry fresh tea (not extracted), the original blue colour of the liquid is found on the second day to have been changed into a greenish blue, and subsequently to a pure green. The leaflets of the fresh (not extracted tea), remain strongly contracted and rolled up even after steeping in the water for weeks, whilst tea which has been previously extracted unrolls perfectly without any previous immersion in water.

The characteristic distinction between extracted and fresh tea is shown by the idioblasts. If microscopic sections of leaves which have been steeped for from 1 to 4 days in a cold saturated solution of copper acetate are touched with a drop of the "liquor ferri acetici" of the Russian Pharmacopœia (specific gravity 1·134 to 1·138), and examined under the microscope, all the histological elements which contain tannin have taken a deep, black-blue colour. The tannins are fixed in their normal places by the previous treatment with copper acetate.

In leaves which have been previously extracted, the cell-walls have been previously permeated by the tannin dissolved in water, whilst in fresh tea they remain colourless, because the tannins are found normally not in the idioblasts, but in the surrounding parenchyma-cells. The shrivelling and the inability to unroll in water the tea-leaves which have not been previously extracted with hot water must depend on the formation of a dense, solid, copper tannate, insoluble in water. It is a kind of tannin which prevents the turgescence of the tissues.

E. Hanausek (*Zeit. f. Nahrungsmittel Untersuchung*) detected the appearance of a green colour also in extracted tea, and in his experiments the idioblasts did not show sharply and consistently the expected microchemical reactions, probably in consequence of the complete exhaustion of the leaves. Hanausek's further experiments had the purpose of determining the refractive index of the infusion of tea as a distinction between extracted and recent tea.

As these experiments are not completed, and as the determination of the proportion of extract afford a more certain basis than the indices of refraction which do not differ very widely among themselves, we must refer to the original.—*Pharm. Zeit. Russland's.*

## THE MICROCHEMICAL RECOGNITION OF SULPHUR.

### Notice on the Use of Gaseous Reagents, especially the Vapour of Bromine, in Microchemical Analysis.

By F. EMICH.

The author's purpose is to show that in many cases gaseous reagents may be advantageously used in microchemical analysis. Bromine vapour seems capable of various applications as a convenient and energetic oxidising agent. It is recommended if sulphur, whether free or as a metallic sulphide, is to be shown in the form of gypsum.

The substance to be tested is moistened with solution of calcium chloride (concentration from 5 to 25 per cent), and exposed to vapours of bromine, the port-object, with the drop downward, being laid over a bottle containing saturated bromine water. The sulphur (of course with a preliminary formation of bromine sulphide) is converted into sulphuric acid, which produces with the calcium chloride the characteristic needles of gypsum.

With free sulphur, or finely-divided sulphides, as obtained by precipitation, the oxidation is so rapid that an exposure to the fumes of bromine for three to five minutes suffices for producing abundant formation of gypsum. Natural or fused sulphides are attacked more slowly, but after trying more than fifty I have met with none which did not yield calcium sulphate on sufficiently prolonged exposure to the vapour of bromine. Hence, without doubt, the reaction may be characterised as universally applicable. In many cases it may prove superior to fusion with soda and saltpetre, which has been recommended in the *Zeit. Anal. Chemie*, xxx., 166.

As in this process we add no more liquid to the original drop, the gypsum crystallises rapidly. With a slight dust of "milk of sulphur" the reaction succeeds perfectly, except too much solution of calcium chloride has been taken. I have dissolved 0·5 grm. pure sulphur in 50 c.c. of pure carbon disulphide. The residue of one m.grm. of the solution, *i.e.*, 0·001 m.grm. sulphur, gave the reaction readily. If the above sulphur solution was diluted to the 50th, one m.grm. of the new solution evaporated down on the port-object, the scarcely perceptible speck of sulphur (0·00003 m.grm.), touched with the solution of calcium chloride by means of a platinum needle, and then exposed to bromine, numerous tufts of crystals of gypsum were detected with a magnifying power of 300 diameters. Hence, the 50,000th part of a m.grm. of sulphur can be certainly recognised by this test.

If a grain of mustard-seed is steeped over night in a solution of calcium chloride, and then exposed for some hours to the fumes of bromine, it is found covered with crystals of gypsum.

In order to convert an arsenical mirror into magnesium ammonium arseniate, it is formed on a port-object, treated with moist vapour of bromine, and then after the addition of a trace of solution of magnesium sulphate, again fumed with dilute ammonia.

If we mix a solution of potassium iodide with a few granules of starch, and treat it with the vapour of red nitric acid, it is easy to obtain the blue colour with 0·0001 m.grm. KI (containing 0·00007 m.grm. I).—*Zeit. Anal. Chemie*, xxxii., p. 163.

## DETERMINATION OF THE SALTS OF IRON BY AN IODOMETRIC METHOD. APPLICATION OF THE METHOD TO THE DETERMINATION OF IRON IN ORES.

By EDOUARD NIHOUL.

It is known that ferric salts react with potassium iodide in presence of an acid. Under ordinary conditions the reaction is not completed, there remaining potassium iodide undecomposed and ferric salt not reduced to the ferrous state.

M. Duflos proposed to render this transformation quantitative by heating under pressure the mixture of ferric salt, potassium iodide, and hydrochloric acid; the free iodine is then determined in presence of ferrous salts by sodium thiosulphite. But this procedure is not merely scarcely practicable, but it often gives discordant results. We think it more convenient to eliminate the iodine by distillation as it is formed, and to determine it in the absence of ferrous salts. In our first attempts we nevertheless operated in presence of these salts. The operation is effected by means of an arrangement analogous to that which we made use of for the determination of nitrates and chlorates.

The apparatus consists of a flask for fractionated distillation, closed with a tubulated stopper in which is passed a tube bifurcated at its upper end. One of the branches of the tube is in communication with an apparatus for carbonic acid, whilst the other serves for the introduction of the potassium iodide. This latter may be ultimately put in communication either with a steam-pipe or an apparatus for gaseous hydrochloric acid. The products of distillation are received in a Volhard's condenser, containing a solution of potassium iodide.

The ferric salt is introduced either as a solid or in solution into the apparatus for fractionated distillation, hydrochloric acid is added, and it is dissolved by the aid of heat if needful. The apparatus is cleared from the air which it contains by means of a current of carbonic anhydride. When all the air is expelled, we introduce a small excess of a rather concentrated solution of potassium iodide by means of a small pipette, the tube of which is placed in communication with the free branch of the bifurcated tube. The contents of the flask are heated to ebullition, still keeping up a slight current of carbonic anhydride.

After ten to fifteen minutes the iodine has passed almost in totality into the Volhard flask, where it is condensed. The contents of the flask are added to the distillate, and the iodine is determined in the total liquid by a solution of sodium thiosulphite, normal or decinormal, according as we operate on a smaller or larger quantity of iron. The ferric salts react with potassium iodide according to the following formula—

$$Fe_2Cl_6+2KI=Fe_2Cl_4+2KCl+I_2.$$

0·4416 of iron corresponds to 1 part of iodine.

Care must be taken in the application of this method to allow the contents of the flask to cool, on distillation, with exclusion of air, in a current of carbonic anhydride. The determination should be made very rapidly so as to prevent the possible return of a part of the ferrous salts to the ferric state. 50 c.c. of a ferric solution containing 4 grms. iron per litre gave 0·1996 of iron in place of 0·200; 10 c.c. of the same solution gave 0·0401 in place of 0·0400.

In order to verify the accuracy of this process, we executed under the same conditions a new qualitative operation, which showed the absence of ferric salts in the flask after distillation of two-thirds of the original solution. We may avoid adding the contents of the flask to that of the condenser for the determination of the iodine. For this purpose it is sufficient to eliminate the iodine completely by distillation. This may be effected by several procedures.

(I.) We add concentrated hydrochloric acid in several portions during the operation, especially at the end. Under these conditions the excess of potassium iodide is decomposed and transformed into chloride, the iodine is no longer retained in the apparatus, and distils with the hydriodic acid formed during the reaction.

A practical trial under these conditions on the distillate alone gave 0·0395 grm. in place of 0·0400 grm. of iron employed. Instead of using hydrochloric acid in a concentrated solution, it is advantageous to make use of gaseous hydrochloric acid if we have a suitable apparatus at hand.

(II.) We may employ a current of steam. However, the distillation of iodine is slow and is not complete as long as there remains undecomposed potassium iodide, in consequence of the energy with which this salt retains iodine. It has no real advantage except in cases where the excess of potassium iodide has been previously destroyed. In the use of the method the following precautions should be taken:—

1. Refrigerate the Volhard condenser so as to condense the vapours of iodine rapidly.

2. Make use, as far as possible, of stoppers which have been used two or three times; the action of iodine vapours on a new stopper constitutes an appreciable loss when operating upon small quantities.

3. Place after the Volhard flask a second similar condenser in cases where we operate upon large quantities of ferric salts.

### *Determination in Ores.*

*The Iron is Present in the Ferric State.*—We weigh from 0·3—0·5 grm. of the ore finely powdered, and introduce it into the flask for fractionated distillation. We add 25 c.c. of concentrated hydrochloric acid, and then introduce a slow current of gaseous hydrochloric acid, heating meanwhile almost to ebullition. In this manner the hydrochloric acid is always kept at its maximum of concentration, and the solution is made very rapidly. The apparatus is then put in connection with Volhard's condenser. A current of carbonic anhydride is then introduced. Then we pour into the flask the solution of potassium iodide in slight excess, and heat to ebullition. When the chief part of the iodine has been distilled, small quantities of gaseous hydrochloric acid are repeatedly introduced to the residue; and when all the iodine has disappeared it is determined in the distillate by means of solution of thiosulphate. It is sometimes advantageous to introduce into the flask before the action a small crystal of potassium iodide, the hydriodic acid considerably facilitating the solution of the ore. We may even introduce at the outset all the potassium iodide necessary for the reaction. In these two latter cases care must be taken to sweep out the apparatus with carbonic anhydride in order to avoid the action of oxygen upon the hydriodic acid set at liberty.

The assay of an ore performed with and without the previous addition of potassium iodide, has given us successively, 51·4 and 51·9 per cent. The analysis by the permanganate process gave 51·7 per cent.

*The Iron is in the Ferrous State, or simultaneously in the Ferrous and Ferric States.*—We dissolve, as above, with gaseous hydrochloric acid, but without the previous addition of potassium iodide. When the solution is completed, we add some crystals of potassium chlorate or permanganate, and we continue whilst maintaining the liquid at ebullition to introduce a current of hydrochloric acid until the chlorine has entirely disappeared. The apparatus is then swept out with carbonic anhydride, the flask is re-connected to the condenser, the potassium iodide is introduced, and the operation is completed as in the former case.

### *Supplementary Note on the Iodometric Determination of Iron in Ores.*

The only difficulty presented by the process above described lies in the complete expulsion of the iodine from the flask for fractionated distillation, in which the reaction is effected between the ferric salt and the potassium iodide. We have indicated the two following methods as enabling us to reach this result.

1. Destroy the excess of potassium iodide by hydrochloric acid, as the potassium iodide obstinately retains the last portions of iodine.

2. Introduce a current of steam into the apparatus at the end of the operation. Under the conditions of the experiment this latter process offers no real advantage.

At the advice of Prof. de Koninck we have substituted hydriodic acid in solution for potassium iodide. Under such conditions the iodine is no longer retained so obstinately in the flask, and it may be easily expelled at the end of a few minutes by a current of steam. The following experiments demonstrate this. They have been made with quantities of a solution of known strength accurately measured.

| Iron taken. | Iron found. |
|---|---|
| 0·0278 | 0·0276 |
| 0·0557 | 0·0557 |
| 0·0835 | 0·0834 |

We have further satisfied ourselves that the contents of the flask, after distillation, no longer contained a trace of free iodine. In the application of the method to the analysis of ores, the use of hydriodic acid presents also the advantage of avoiding the use of gaseous hydrochloric acid. In fact, the solution of the ore may be very well effected by a mixture of concentrated hydrochloric and hydriodic acid. This method can evidently be used only if the iron in the substance to be analysed is entirely in the ferric state.

Commercial hydriodic acid often contains small quantities of free iodine. Its proportion of iodine must therefore be determined at the moment of the operation so as to be taken into account in the final result; or this iodine may be made to disappear by the addition of stannous chloride in the proportion exactly necessary.

The commercial product, obtained by means of phosphorus, sometimes gives off a faint odour of phosphamine, but we have found that this has no influence on the accuracy of the results.—*Revue Universelle des Mines et de la Metallurgie*, xxi., No. 1.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, April 14th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In our previous report for the month of February we called attention to the degree of colour-tint of the water then being supplied, which, though insufficient to be noticeable in small bulks of the water, became very apparent on its being submitted to definite colorimetric examination. During the first ten days or so of the succeeding month of March, while the river still continued in flood, the degree of colour-tint of the supply, taken notice of in our previous report, did not manifest any appreciable reduction; but during the remainder of the month, alike in degree of freedom from colour-tint and in the smallness of the amount of organic matter present, the condition of the water supply was unexceptional.

In the supply for the entire month, indeed, taking the Thames-derived water for illustration, the mean proportion of organic carbon present was found to be 0·172 part in 100,000 parts of the water, with a maximum of 0·272 part in any single sample examined—as against a mean of 0·185 and maximum of 0·286 part in the previous three months' supply. Again the mean amount of oxygen required to oxidise the organic matter present was 0·057 grain per gallon of water, as against a mean of 0·063 grain per gallon in the previous three months' supply.

Of the entire 182 samples of water examined during the month, three were recorded as wanting in brightness, and one as being slightly turbid, the remaining 178 samples being well filtered, clear, and bright.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

### ON THE
## DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

(Continued from p. 185).

### *The Weights.*

The object of the investigation being to ascertain the *ratio* of densities of water and of certain gases under given conditions, the absolute values of the weights employed is evidently a matter of indifference. This is a point which I think it desirable to emphasise, because v. Jolly, in his, in many respects, excellent work upon this subject (*Munich Acad. Trans.*, vol. xiii., II., 49, 1880), attributes a discrepancy between his final result for oxygen and that of Regnault to a possible variation in the standard of weight. On the same ground we may omit to allow for the buoyancy of the weights as used in air, since only the *variations* of buoyancy, due, for example, to changing barometer, could enter; and these affect the result so little that they may safely be neglected.†

But, while the absolute values of the weights are of no consequence, their relative values must be known with great precision. The investigation of these over the large range required (from a kilogrm. to a centigrm.) is a laborious matter, but it presents nothing special for remark. The weights quoted in this paper are, in all cases, corrected, so as to give the results as they would have been obtained from a perfectly adjusted system.

### *The Water Contents of the Globe.*

The globe being packed in finely-divided ice, was filled with boiled distilled water up to the level of the top of the channel through the plug of the tap, that is, being itself at 0°, was filled with water also at 0°. Thus charged the globe had now to be weighed; but this was a matter of some difficulty, owing to the very small capacity available above the tap. At about 9° there would be a risk of overflow. Of course the water could be retained by the addition of extra tubing, but this was a complication it was desired to avoid. In February, 1892, during a frost, an opportunity was found to effect the weighing in a cold cellar at a temperature ranging from 4° to 7°. The weights required (on the same side of the balance as the globe and its supports) amounted to 0·1822 grm. On the other side were other weights whose values did not require to be known so long as they remained unmoved during the whole series of operations. Barometer (corrected) 758·9 m.m.; temperature 6·3°.

A few days later the globe was discharged, dried, and replaced in the balance with tap open. 1834·1701 grms. had now to be associated with it in order to obtain equilibrium. The difference,—

$$1834·170 - 0·182 = 1833·988,$$

represents the weight of the water less that of the air displaced by it. The difference of atmospheric conditions was sufficiently small to allow the neglect of the *variation* in the buoyancy of the glass globe and of the brass counterpoises.

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* A Paper read before the Royal Society.

† In v. Jolly's calculations the buoyancy of the weights seems to be allowed for in dealing with the water, and neglected in dealing with the gases. If this be so, the result would be effected with a slight error, which, however, far exceeds any that could arise from neglecting buoyancy altogether.

It remains to estimate the actual weight of the air displaced by the water under the above mentioned atmospheric conditions. It appears that, on this account, we are to add 2·314, thus obtaining—

1836·30

as the weight of the water at 0° which fills the globe at 0°.

A further small correction is required to take account of the fact that the usual standard density is that of water at 4° and not at 0°. According to Broch (Everett's "C.G.S. System of Units"), the factor required is 0·99988, so that we have—

$$\frac{1836{\cdot}30}{0{\cdot}99988} = 1836{\cdot}52$$

as the weight of water at 4° which would fill the globe at 0°.

### *Air.*

Air drawn from outside (in the country) was passed through a solution of potash. On leaving the regulating tap it traversed tubes filled with fragments of potash, and a long length of phosphoric anhydride, followed by a filter of glass wool. The arrangements beyond the regulating tap were the same for all the gases experimented upon. At the close of the filling it was necessary to use a condensing syringe in order to force the pressure up to the required point, but the air thus introduced would not reach the globe. It may be well to give the results for air in some detail, so as to enable the reader to form a judgment as to the degree of accuracy attained in the manipulations.

| Date. | Globe empty. | Globe full. | Temp. of manometer. | Correction to 15°. | Corrected to 15°. |
|---|---|---|---|---|---|
| 1892. | | | | | |
| Sept. 24 | 2·90941 | | | | |
| ,, 27 | — | 0·53327 | 17·8 | −0·00112 | 0·53219 |
| ,, 28 | 2·90867 | — | | | |
| ,, 29 | — | 0·53271 | 15·7 | −0·00028 | 0·53243 |
| Oct. 1 | 2·90923 | — | | | |
| ,, 3 | — | 0·53151 | 12·7 | +0·00093 | 0·53244 |
| ,, 4 | 2·90872 | | | | |
| | | Tap re-greased. | | | |
| ,, 7 | 2·91036 | | | | |
| ,, 8 | — | 0·53296 | 12·4 | +0·00105 | 0·53401 |
| ,, 10 | 2·91056 | | | | |
| ,, 11 | — | 0·53251 | 11·8 | +0·00129 | 0·53380 |
| ,, 12 | 2·91039 | | | | |
| ,, 13 | — | 0·53201 | 11·0 | +0·00161 | 0·53362 |
| ,, 14 | 2·91043 | | | | |
| ,, 15 | — | 0·53219 | 10·6 | +0·00177 | 0·53396 |

The column headed "globe empty" gives the (corrected) weights, on the side of the working globe, required for balance. The third column gives the corresponding weights when the globe was full of air, having been charged at 0° and up to the pressure required to bring the mercury in the manometer into contact with the two points of the measuring rod.

This pressure was not quite the same on different occasions, being subject to a temperature correction for the density of mercury and for the expansion of the iron rod. The correction is given in the fifth column, and the weights that would have been required, had the temperature been 15°, in the sixth. The numbers in the second and sixth columns should agree, but they are liable to a discontinuity when the tap is re-greased.

In deducing the weight of the gas we compare each weighing "full" with the mean of the preceding and following weights "empty," except in the case of October 15, when there was no subsequent weighing empty. The results are given in the Table (see top of next column).

There is here no evidence of the variation in the density of air suspected by Regnault and v. Jolly. Even if we include the results for September 27th, obviously affected by irregularity in the weights of the globe empty, the extreme difference is only 0·4 m.grm., or about $\frac{1}{6000}$th part.

| | | |
|---|---|---|
| September | 27 | 2·37686 |
| ,, | 29 | 2·37651 |
| October | 3 | 2·37653 |
| ,, | 8 | 2·37646 |
| ,, | 11 | 2·37668 |
| ,, | 13 | 2·37679 |
| ,, | 15 | 2·37647 |
| Mean.. | | 2·37661 |

To allow for the contraction of the globe (No. 14) when weighed empty, discussed in my former papers, we are to add 0·00056 to the apparent weight, so that the result for air becomes—

2·37717.

This is the weight of the contents at 0° and under the pressure defined by the manometer gauge at 15° of the thermometer. The reduction to standard conditions is, for the present, postponed.

### *Oxygen.*

This gas has been prepared by three distinct methods (*a*) from chlorates, (*b*) from permanganate of potash, (*c*) by electrolysis.

In the first method, mixed chlorates of potash and soda were employed, as recommended by Shenstone, the advantage lying in the readier fusibility. The fused mass was contained in a Florence flask, and during the wash out was allowed slowly to liberate gas into a vacuum. After all air had been expelled, the regulating tap was closed, and the pressure allowed gradually to rise to that of the atmosphere. The temperature could then be pushed without fear of distorting the glass, and the gas was drawn off through the regulating tap. A very close watch over the temperature was necessary to prevent the evolution of gas from becoming too rapid. In case of excess, the superfluous gas was caused to blow off into the atmosphere, rather than risk imperfect action of the potash and phosphoric anhydride. Two sets of five fillings were effected with this oxygen. In the first set (May, 1892) the highest result was 2·6272, and the lowest 2·6266; mean, 2·62691. In the second set (June, July, 1892) the highest result was 2·6273, and the lowest 2·6267, mean 2·62693.

The second method (*b*) proved very convenient, the evolution of gas being under much better control than in the case of chlorates. The re-crystallised salt was heated in a Florence flask, the wash-out, in this case also, being facilitated by a vacuum. Three fillings gave satisfactory results, the highest being 2·6273, the lowest 2·6270, and the mean 2·62714. The gas was quite free from smell.

By the third method I have not as many results as I could have wished, operations having been interrupted by the breakage of the electrolytic generator. This was, however, of less importance, as I had evidence from former work that there is no material difference between the oxygen from chlorates and that obtained by electrolysis. The gas was passed over hot copper, as detailed in previous papers. The result of one filling, with the apparatus as here described, was 2·6271. To this may be added the result of two fillings obtained at an earlier stage of the work, when the head of the manometer was exhausted by an independent Sprengel pump, instead of by the Töppler. The value then obtained was 2·6272. The results stand thus:—

| | |
|---|---|
| Electrolysis (2), May, 1892 .. .. .. | 2·6272 |
| ,, (1), ,, .. .. .. | 2·6271 |
| Chlorates (5), May, 1892 .. .. .. | 2·6269 |
| ,, (5), June, 1892 .. .. .. | 2·6269 |
| Permanganate (3), January, 1893 .. | 2·6271 |
| Mean.. .. .. .. .. .. .. | 2·62704 |
| Correction for contraction .. | 0·00056 |
| | 2·62760 |

It will be seen that the agreement between the different methods is very good, the differences, such as they are, having all the appearance of being accidental. Oxygen prepared by electrolysis is perhaps most in danger of being light (from contamination with hydrogen), and that from chlorates of being abnormally heavy.

### *Nitrogen.*

This gas was prepared, in the usual manner, from air by removal of oxygen with heated copper. Precautions are required, in the first place, to secure a sufficient action of the reduced copper, and, secondly, as was shown by v. Jolly, and later by Leduc, to avoid contamination with hydrogen which may be liberated from the copper. I have followed the plan, recommended by v. Jolly, of causing the gas to pass finally over a length of unreduced copper. The arrangements were as follows:—

Air drawn through solution of potash was deprived of its oxygen by reduced copper contained in a tube of hard glass heated by a large flame. It then traversed a U-tube, in which was deposited most of the water of combustion. The gas, practically free, as the event proved, from oxygen, was passed, as a further precaution, over a length of copper heated in a combustion furnace, then through strong sulphuric acid,* and afterwards back through the furnace over a length of oxide of copper. It then passed on to the regulating tap, and thence through the remainder of the apparatus, as already described. In no case did the copper in the furnace, even at the end where the gas entered, show any signs of losing its metallic appearance.

Three results, obtained in August, 1892, were—

| | |
|---|---|
| August 8.. .. .. | 2·31035 |
| ,, 10.. .. .. | 2·31026 |
| ,, 15.. .. .. | 2·31024 |
| Mean .. .. | 2·31028 |

To these may be added the results of the two special experiments made to test the removal of hydrogen by the copper oxide. For this purpose a small hydrogen generator, which could be set in action by closing an external contact, was included between the two tubes of reduced copper, the gas being caused to bubble through the electrolytic liquid. The quantity of hydrogen liberated was calculated from the deflection of a galvanometer included in the circuit, and was sufficient, if retained, to alter the density very materially. Care was taken that the small stream of hydrogen should be uniform during the whole time (about 2½ hours) occupied by the filling, but, as will be seen, the impurity was effectually removed by the copper oxide.† Two experiments gave—

| | |
|---|---|
| September 17 .. .. | 2·31012 |
| ,, 20 .. .. | 2·31027 |
| Mean .. .. | 2·31020 |

We may take as the number for nitrogen—

| | |
|---|---|
| | 2·31026 |
| Correction for contraction .. | 56 |
| | 2·31082 |

Although the subject is not yet ripe for discussion, I cannot omit to notice here that nitrogen prepared from ammonia, and expected to be pure, turned out to be decidedly lighter than the above. When the oxygen of air is burned by excess of ammonia, the deficiency is about $\frac{1}{1000}$th part.‡ When oxygen is substituted for air, so that all (instead of about one-seventh part) of the nitrogen is derived from ammonia, the deficiency of weight may amount to ½ per cent. It seems certain that the abnormal lightness cannot be explained by contamination with hydrogen, or with ammonia, or with water, and everything suggests that the explanation is to be sought in a dissociated state of the nitrogen itself. Until the questions arising out of these observations are thoroughly cleared up, the above number for nitrogen must be received with a certain reserve. But it has not been thought necessary, on this account to delay the presentation of the present paper, more especially as the method employed in preparing the nitrogen for which the results are recorded is that used by previous experimenters.

(To be continued).

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* There was no need for this, but the acid was in position for another purpose.

† Much larger quantities of hydrogen sufficient to reduce the oxide over several centimetres, have been introduced without appreciably altering the weight of the gas.

‡ *Nature*, vol. xlvi., p. 512.

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## ON THE DETERMINATION OF IODINE IN HALOID SALTS BY THE ACTION OF ARSENIC ACID.*

By F. A. GOOCH and P. E. BROWNING.

Three years ago we demonstrated (*American Journal of Science*, xxxix., p. 188) the possibility of determining iodine in mixtures of alkaline chlorides, bromides, and iodides, with rapidity and exactness, by taking advantage of the behaviour of arsenic acid toward the haloid salts in presence of sulphuric acid of definite strength. We showed in brief that when amounts of potassium iodide ranging from 0·005 grm. to 0·5 grm. were dissolved in 100 c.m.$^3$ of water containing 2 grms. dihydrogen potassium arseniate and 20 c.m.$^3$ of a mixture of sulphuric acid with water in equal volumes, the entire amount of iodine was expelled on boiling down the solution from 100 c.m.$^3$ to 35 c.m.$^3$; and further, that arsenic, reduced to the arsenious condition to an amount the exact equivalent of the iodine liberated, remained in solution and was determinable, after neutralisation of the acid, in presence of an alkaline bicarbonate, by titration against standard iodine according to Mohr's classical method. We studied carefully the behaviour of alkaline bromides and chlorides under identical conditions, and determined that 0·5 grm. of potassium bromide acted upon the mixture of arseniate and acid to the extent of reducing arsenic equivalent to 0·0008 grm. of iodine, and that 0·5 grm. of sodium chloride did not reduce arsenic, but did cause, under the conditions, a volatilisation proportional to the amount of arsenious oxide present, the loss amounting at the most —when 0·56 grm. of the iodide was present to exert its reducing action upon the arsenic—to 0·0011 grm. We showed, furthermore, that these maximum errors, due to the action of bromides and chlorides, though not large and tending to neutralise one another when both bromides and chlorides are present, may be eliminated by the application of a numerical correction to the results whenever the amounts of bromide and chloride present become known.

Recently Messrs. Friedheim and Meyer (*Zeitsch. f. Anorg. Chem.*, i., p. 407) have recognised the value of our reaction, and applied it to the elimination of iodine from mixtures of haloid salts. They have, however, taken issue with us (unadvisedly, as we think) as to matters of detail. They have, in the first place, put themselves upon record as being unable to titrate arsenious oxide by iodine in alkaline solution under the conditions of our process. They account for their failure by the wholly unsupported hypothesis that the iodine reaction is unavailable in presence of the amounts of salts present, and modify the treatment by distilling, collecting the iodine in the distillate, and determining it by the thiosulphate method, thus introducing complexity of

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* *American Journal of Science*, xlv., April, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

apparatus and manipulation, and sacrificing the simplicity and rapidity which are chief advantages of our process. Had they read our paper with intelligent care it must have been evident that we had given special attention to the question of the influence of the salts present upon the iodine reaction; for we expressly stated that "due correction was made for the amount of iodine necessary to develop the test-colour in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide—the correction amounting to a single drop more of the decinormal iodine than was required to produce the end reaction in the same volume of pure water containing only the starch indicator." It is obvious that such errors as 0·003 to 0·006 grm., which Messrs. Friedheim and Meyer found even in the absence of bromides and chlorides, are not explicable by the action of the salts which we used. Our errors ranged under like conditions from 0·0009 grm. – to 0·0003 grm. +, with a mean error in nine determinations of 0·0002 grm. –.

Everybody knows that the starch iodide test is most delicate in acid solutions and in presence of combined iodine, but Mohr's method of titrating arsenious oxide and iodine against one another in alkaline solution is sufficiently delicate for very exact work, provided only that the alkali in excess is in the form of the bicarbonate, that the starch emulsion is used in abundance, and that the volumes of solutions titrated are regulated to low and uniform measure. In many determinations of iodine made by our method at different times and with different materials, it has never been our ill-fortune to chance upon results so extraordinary as those of Messrs. Friedheim and Meyer, though we have met in the course of our work with potassium arseniate so contaminated with nitrates as to be unfit for use and with alkaline hydroxides too impure to employ. Most analytical processes depend for their exactness upon the use of proper materials; ours is no exception to the rule in this regard.

As to the correctness of the main reaction there appears to be no difference of opinion between Messrs. Friedheim and ourselves. We have, therefore, taken the pains, perhaps unnecessarily, to make experiments in which the estimation of the iodine of the same identical portions is effected both in the distillate and in the residue, in order that the two modes of estimation may be brought into direct comparison. It is scarcely needful to add that we took care to work with pure reagents. The potassium iodide, like that which we employed in our former investigation, was prepared by acting with re-sublimed iodine upon an excess of iron wire, pouring off the solution from the iron when the colour of iodine had vanished, adding iodine equal to one-third the amount of that originally used, pouring the filtered liquid into a boiling solution of the calculated equivalent of potassium carbonate (from the bicarbonate), and filtering off the precipitated magnetic oxide of iron. The slightly alkaline solution thus made, containing approximately 2 grms. of potassium iodide in 100 c.m.$^3$, and free from chlorine and bromine, was standardised by precipitating the iodine from weighed portions in the form of silver iodide and weighing upon asbestos. The other reagents—the sulphuric acid, the sodium hydroxide, the acid potassium carbonate, the dihydrogen potassium arseniate—when present in the proportions used in our process and mixed with 5 c.m.$^3$ of clear starch solution prepared by Gastine's formula (*Bull. Soc. Chim.*, l., 172) (5 grms. starch, 0·01 $HgI_2$, 1 litre of water) gave the starch blue with a single drop of decinormal iodine at all dilutions below 300 c.m.$^3$. The results of these experiments are given in the accompanying Table.

| | Iodine taken in form of KI. | Iodine found in residue by our method. | Iodine found in distillate by $As_2O_3$. | Iodine found in distillate by $Na_2S_2O_3$. | Error in residue. | Error in distillate. |
|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Grm. | Grm. |
| 1. | 0·4054 | 0·4052 | — | — | 0·0002 – | — |
| 2. | 0·4057 | 0·4055 | — | — | 0·0002 – | — |
| 3. | 0·4054 | 0·4052 | — | — | 0·0002 – | — |
| 4. | 0·4054 | 0·4052 | — | — | 0·0002 – | — |
| 5. | 0·4042 | 0·4046 | 0·4046 | — | 0·0004 + | 0·0004 + |
| 6. | 0·4050 | 0·4052 | 0·4040 | — | 0·0002 + | 0·0010 – |
| 7. | 0·4050 | 0·4052 | — | 0·4039 | 0·0002 + | 0·0011 – |
| 8. | 0·4058 | 0·4052 | — | 0·4051 | 0·0006 – | 0·0007 – |
| 9. | 0·4054 | 0·4046 | — | 0·4051 | 0·0008 – | 0·0003 – |
| 10. | 0·4042 | 0·4046 | — | 0·4039 | 0·0004 + | 0·0003 – |
| 11. | 0·4055 | 0·4052 | — | 0·4057 | 0·0003 – | 0·0002 + |

Experiments 1 to 4 were made exactly in accordance with the directions of our former paper, the mixtures being simply boiled in an Erlenmeyer flask trapped to prevent mechanical loss by hanging in the neck of the flask, with the larger end downward, a straight, two-bulbed drying tube cut off so as to leave the larger tube about 4 c.m. in length. These four experiments all gave the same result, which differed from the theory by 0·0002 grm. –. The mixtures of the remaining experiments were treated in a flask connected with a cooled receiver and absorption tubes for condensing the distilled iodine (all joints being of glass and carefully ground), and carbon dioxide was passed through the apparatus in slow current to facilitate the transfer of iodine and quiet boiling. In experiments 5 and 6 the iodine was received in an alkaline solution of standard arsenious oxide, and titration was effected with standard iodine after addition of starch. The residue was treated by our method. It will be observed that the residues, which contain the large amounts of salts, yield results by titration practically identical with those obtained by treating the distillates which do not contain the large masses of salts. In experiments 7 to 11 the iodine distilled was received in potassium iodide and estimated by standard sodium thiosulphate, itself standardised against the iodine whose value in terms of the standard arsenious oxide was also known. The residues were treated by our method. It is evident that the errors of both processes of treatment are reasonably small (respectively 0·0001 grm. – and 0·0004 grm. – in the average), with what difference there is in favour of our treatment of the residues. Our process is incomparably the more convenient and rapid. We do not doubt that Messrs. Friedheim and Meyer could have obtained equally good results had they worked with pure reagents.

Messrs. Friedheim and Meyer disagree with us also as to the degree of concentration of the liquid necessary to insure the complete expulsion of iodine, and as to the effect of the concentration upon bromides present—points to which we gave particular attention in our former paper. We showed that, in general, upon boiling a mixture of iodide with sulphuric acid, and the arseniate diluted with water, the amount of iodine removed depended upon the proportion of the sulphuric acid to the final volume of the whole liquid, it being plainly shown that even after the liquid had lost the colour of free iodine in the process of concentration, it was still possible to detect combined iodine. Further concentration and, to some extent, dilution and repetition of the concentration to the former point tend to set free the residual iodine.

In experimenting upon the proportions of acid most convenient for the work, we found that a solution made up to contain 0·5 grm. of potassium iodide, 2 grms. of dihydrogen potassium arseniate, and 20 c.m.$^3$ of the sulphuric acid mixture (1 : 1 by volume) retained when boiled down to 40 c.m.$^3$ no determinable free iodine, and but the faintest trace of combined iodine, while at 35 c.m.$^3$ the liquid was free from iodine in any form. Upon experimenting as to the behaviour of mixtures of chlorides and iodides, we found that 0·5 grm. of sodium chloride added to the mixture containing 0·5 grm. of the iodide occasioned at 40 c.m.$^3$ a maximum loss of arsenious chloride equivalent to 0·0004 grm. of the oxide, or to 0·0008 grm. at 30 c.m.$^3$; and that the loss as a matter of course is less as the amount of iodide present (and consequently the arsenious oxide formed) is diminished.

We found that 0·5 grm. of potassium bromide treated in similar manner occasioned no loss of arsenious bromide, but did induce at 35 c.m.$^3$ reduction of the arsenic acid amounting to 0·0005 grm. of iodine. Smaller amounts of bromide produced proportionately smaller effects, but concentration even a little below 35 c.m.$^3$ was likely to be productive of serious error. We fixed upon 35 c.m.$^3$, therefore, as the ideal concentration for removing iodine from unknown mixtures with chlorides and bromides, but expressly stated that failure to concentrate below 40 c.m.$^3$ introduces no appreciable error, while great care should be taken not to press the concentration below 35 c.m.$^3$ on account of the danger of bringing about the reduction of the arsenic by the bromide.

Messrs. Friedheim and Meyer contend that the reduction of volume under the conditions should not be pressed beyond 50 c.m.$^3$ at the most, and cite in proof experiments in which potassium bromide in amounts less than half as great as those which we used caused an error on concentration to 35 c.m.$^3$, equivalent to five or six milligrms. of iodine. They recommend boiling from 150—50 c.m.$^3$ to remove the iodine without disturbing bromine. Our former experiments are sufficiently definite upon these points. We have, however, determined directly and quantitatively the amounts of iodine remaining unexpelled when solutions are boiled from 150—50 c.m.$^3$ and found, in certain experiments, in which the additional iodine expelled in concentrating from 50—35 c.m.$^3$ was collected in potassium iodide and estimated with sodium thiosulphate, that about 0·0013 grm. remained when 0·5 grm. of potassium iodide was originally taken, and 0·0003 grm. when 0·25 grm. of the iodide was present at the first. It is evident, therefore, that concentration to 50 c.m.$^3$ is not sufficient when the maximum amount of iodide may be present. We have also made certain experiments—recorded below—in which the bromine liberated at different degrees of concentration was collected in potassium iodide and estimated by the iodine set free. In our former work we inferred the loss of bromine from the effects upon the arsenic acid in the residues. In these experiments solutions of potassium bromide (free from iodine), with 20 c.m.$^3$ of sulphuric acid (1 : 1), and 2 grms. of dihydrogen potassium arseniate were boiled down in a flask connected by ground glass joints with a cooled receiver containing potassium iodide, and the iodine set free was estimated by standard sodium thiosulphate.

| KBr taken. | Initial volume. | Final volume. | Bromine in distillate. |
|---|---|---|---|
| Grm. | C.m.$^3$ | C.m.$^3$ | Grm. |
| 0·5 .. .. .. .. | 150 | 50 | trace |
| | 50 | 40 | trace |
| | 40 | 35 | 0·0004 |
| 0·5 .. .. .. .. | 50 | 31 | 0·0010 |
| | 31 | 26 | 0·0064 |
| | 26 | 23 | 0·0072 |
| 0·25.. .. .. .. | 45 | 40 | none |
| | 40 | 31 | 0·0004 |
| | 31 | 27 | 0·0010 |
| 0·25.. .. .. .. | 50 | 35 | 0·0003 |
| 0·1 .. .. .. .. | 50 | 30 | 0·0003 |

From these results, which confirm very closely those obtained by an examination of the residues and recorded in our former paper, it is evident that the concentration may go under the most unfavourable conditions—when the maximum amount of bromide is present—to 40 c.m.$^3$ without loss and to 35 c.m.$^3$ with small loss. As we stated in our former paper, concentration below 35 c.m.$^3$ should be avoided.

In our former paper we showed that the iodine could be determined in unknown mixtures of sodium chloride, potassium bromide, and potassium iodide taken in amounts not exceeding 1·5 grm. (in which, however, neither individual salt was present in amount exceeding 0·5 grm.) with a maximum error ranging from 0·0013 grm. − to 0·0016 grm. +. We showed, further, that when the amounts of chloride and bromide present were known also, a correction for the action of these salts might be applied, which reduced the maximum errors to 0·0010 grm. − and 0·0008 grm. +, and gave a mean error of 0·0001 grm. − for twenty-six determinations.

In conclusion, we affirm the correctness of our former work, and reiterate our former directions without change.

## NOTICES OF BOOKS.

*Practical Treatise on Chemical Analysis and Toxicological Researches* (Traite Pratique d'Analyse Chimique et de Recherches Toxicologique). By G. Guerin, Professor attached to the Faculty of Medicine at Nancy. Paris: Georges Carré, 1893. 8vo., pp. 492.

This work possesses certain very valuable features. In the first section on preliminary trials by the dry way there are a series of tables showing the colouration of borax beads obtained before the blowpipe with the metallic oxide, whilst a similar table shows the reactions obtained with phosphorus salt.

The third part treats of the distinctive characters of different bodies, and gives—at least, where the rarer elements are concerned—the spectroscopic reactions of the substances in question. We notice that in this part the metals are arranged not in their analytical groups, but alphabetically. The non-metallic substances are entitled *more gallico* metalloids. The organic salts, *e.g.*, uric, hippuric, phenic, meconic, &c., are noticed more fully than we generally find in text-books of moderate size.

In addition to the notes on the spectral reactions of the metals, there is a part exclusively devoted to spectral analysis. Here we find a catalogue of the rays of the most important bodies expressed in wave-lengths, figures of different spectroscopes, an account of emission spectra, of the manner of producing spectrum lines, observing and measuring them, the projection of spectra, the use of the electric spark, on absorption spectra, and the manner of their observation.

We find here the interesting fact recorded by M. de Chardonnet that certain persons who had undergone the operation for cataract, *i.e.*, had been deprived of the "crystalline," saw the spectrum prolonged far beyond the violet, which forms the ordinary limit of the visible portion. Physicists explain this phenomenon by assuming that the radiations neither of the extreme red nor of the ultra-violet reach the retina. The aqueous media of the eye would absorb the infra red rays, as does water, and the tissue of the crystalline being fluorescent, absorb the ultra-violet rays, as do all substances which possess this property.

After instructions for observing the absorption-spectra and an account of the absorption bands of chlorophyll, of potassium permanganate, and of the salts of didymium and erbium, the author proceeds to describe and figure the characteristic bands of blood. Here the name of Sir G. Stokes is converted into Stockes. A special chapter is devoted to the detection of blood spots. Here mention is made of the "hæmato spectroscope" of M. de Thierry.

Part VI. is devoted to toxicology, prominence being given to arsenic, phosphorus, hydrocyanic acid, chloroform and chloral, and the alkaloids. The methods of Stas and Dragendorff are explained and criticised at length. Next follow the bacterian alkaloids, the ptomaines, and leucomaines. We may here ask whether the time has yet come for the authoritative promulgation of structural formulæ for these bodies? Are they, even if capable of demonstration, in their right place in an analytical treatise?

The reactions of the ordinary alkaloids are fully laid down. The venoms of serpents are mentioned in passing as containing alkaloids, but we do not find any detailed critical description. Much research is here still required, but it cannot be undertaken in Britain, or, indeed, in any part of the British Empire, on account of the agitation stirred up by the bestiarians.

From the alkaloids Prof. Guérin passes to the analysis of potable waters. He admits the faintly blue colour of pure waters if seen in deep masses. He rightly condemns magnesium waters, but he holds that the chemico-physical analysis of waters does not warrant a decision on their hygienic properties without a biological examination.

In the chemical analysis of waters he retains the unsatisfactory procedure of evaporating to dryness at 100° and noting the loss on ignition at a red heat. The shortcomings of this procedure are so well known that they do not need to be here recapitulated. Ammonia and organic nitrogen he determines by Wanklyn's method. For nitrates he gives the methods with brucine, with diphenylamine, and with the sulphophenic reagent of Grandval and Lajoux. We are surprised to find no reference to lead, one of the most dangerous and commonest impurities in potable waters.

The bacteriological examination of drinking-waters is discussed very fully, but there is no reference to the analysis of sewage, of industrial waste-waters, drainage, or urines. Lastly come instructions for the assay of clays and of irons snd steels.

Prof. Guérin's work is upon the whole highly useful, very rich in some directions, though strangely defective in others.

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*Diseases Incident to Workpeople in Chemical and other Industries.* An Address Delivered before the Chemical and Physical Society of University College, London. By Watson Smith. London: Eyre and Spottiswoode, 1893. 8vo., 34 pp. (Second Notice.)

The match-manufacture employs a small number of persons in comparison with the production of alkali, but it must be charged with a much higher proportion of mischief. The manufacture of phosphorus itself is less dangerous than its subsequent elaboration into matches. The special disease which may be produced is necrosis of the jaw. At the works of Messrs. Albright and Wilson, of Birmingham, the largest phosphorus makers in the world, every known precaution for the safety of the workpeople is taken and with success. No girls or young boys are employed, and the cases of necrosis occurring are few, and being at once attended to they are easily cured. The firm state that men of a scrofulous taint or of intemperate habit are most susceptible to the mischief.

In match-making the risk is greater. The number of hands is larger, the phosphorus is much sub-divided, and has consequently much greater opportunity of giving off its vapours. There is a remedy, the exclusive use of the so-called red or amorphous phosphorus in place of the normal white or yellow form. In some countries the use of the latter kind is legally prohibited. But such enactments are too often a dead letter even in Germany, where, according to Prof. Lunge, it is carried on secretly, and will be so until the small match-works,—the so-called house factories—are stopped. Such establishments are much less rampant in England. In Switzerland the match-manufacture is about to be constituted a Government monopoly on purely sanitary grounds. In the small Swiss factories it has actually been customary for the workmen to be paid partly in money and *partly in matches*, reckoned at 30 per cent above their real value!

It is stated, on the authority of the *Chemiker Zeitung*, that the attempts to supersede phosphorus altogether in the match-manufacture have, so far, proved a failure, the matches thus made being too explosive. Perhaps, however, the difficulty may yet be overcome, which is very desirable, since all the phosphorus in existence is wanted as plant-food.

Mr. Watson Smith tells us that in the safety-match department of Messrs. Bryant and May no smell of phosphorus could be recognised. The match-works of the Salvation Army use only amorphous phosphorus and keep up thorough ventilation. The health of the workpeople is satisfactory.

White-lead next claims our attention. Mr. Watson Smith rightly contends that whatever process is used in this manufacture, so long as there is dust there is danger. Even the new white-lead, consisting principally of lead sulphate, cannot be absolutely safe. Lead sulphate is decidedly soluble in ammonium acetate and tartrate, and it is converted into lead carbonate by sodium bicarbonate. Hence, if a person is exposed to the dust of lead sulphate, a draught of the ordinary effervescing beverages may at once produce in his digestive organs the actively poisonous lead carbonate.

We hope that the author's protest against dilute sulphuric acid as a safeguard against lead poisoning will not be generalised so as to form an objection to its use as a prophylactic against cholera and various other tropical diseases,—of course not including yellow fever, the bacillus of which seems to thrive in acid media.

It appears that "workmen employed in factories where arsenic acid and also bichromate of potash are made, especially the former, are subject to blisters and ulcers that precisely resemble those common in syphilitic diseases. The result is that such workmen have often been treated, and wrongly treated, for acute syphilis." It is satisfactory that the demand for arsenic acid has much abated since the Medlock process is no longer exclusively used in the manufacture of magenta.

Carbon disulphide, when inhaled, is a serious poison, and it is the more formidable as its effects have been wrongly ascribed to alcoholic intoxication. Mr. H. L. Terry, a former pupil of the author, has hopes that in the process for vulcanising indiarubber it may soon be superseded by a newly discovered product.

Dr. Weber, of Manchester, gives a simple method of distinguishing the earlier stages of poisoning by carbon disulphide from the effects of alcohol.

The patient is placed in the open air for from five to ten minutes, and is allowed to drink some milk and soda-water. If alcohol has been at work no improvement is perceived, but in the case of carbon disulphide the symptoms disappear very rapidly. It is to be noted that though the "curing" of caoutchouc goods is now conducted in machines, encased and well ventilated, yet "the men attending them frequently carelessly expose themselves to the carbon disulphide vapours escaping in large quantities."

Two tests are here laid down for detecting carbon disulphide in saliva. For the *phenylhydrazine* reaction from 10—15 c.c. of the saliva are shaken up with from 20—25 c.c. of benzene. All the $CS_2$ is taken up by the latter, and on adding to it a few crystals of phenylhydrazine (the free base), a beautiful crop of the crystalline compound is deposited.

The triethylphosphine reaction is obtained by shaking up the saliva with an ethereal solution of triethylinephosphine, $P(C_2H_5)_3$. If $CS_2$ is present a beautiful pink colour appears, due to the formation $(C_2H_5)_3P.CS_2$. If the quantity of $CS_2$ is not too small, a red crystalline deposit of the compound is obtained. According to Dr. Weber, the chief danger from nitrobenzene lies not so much in the preparation of this compound, or in its conversion into anilne, as in the manufacture of metanilic acid and benzidine. It may be pronounced a treacherous poison, as its symptoms appear suddenly and without any warning. Dr. Weber himself seems to have had a rather narrow escape from poisoning by the vapours of aniline.

Cases of arsenical poisoning occur at pigment-works in the manufacture of Schweinfurt green (or Paris green, as it is sometimes called) and of "rose pink"—a preparation of magenta precipitated upon aluminium arsenite.

The proposal to constitute a small consultative committee to advise the Home Secretary on the sanitary bearings of various trades, *if rightly constituted*, would be exceedingly useful.

Mr. Watson Smith's work will, we hope, be widely read and appreciated. It will be a safe guide for journalists.

*Electro-Medical Supplies.* The General Electric Co., Limited, Queen Victoria Street, London.

This catalogue figures and describes an extensive assortment of apparatus for *bona fide* medical and surgical purposes. Practitioners will note here the absence of those alleged wonder-working batteries which have been so much pushed of late by persons scantily acquainted either with electricity or pathology.

*A Summer School of Art and Science.* Edinburgh Summer Meeting. Seventh Session, July 31st to August 26th, 1893.

It is satisfactory to find that this movement promises to be permanent. In the remarks on the "educational purpose of the courses," we note the following passage with especial satisfaction: "Hence the examination method is here definitely abandoned; a keener stimulus, even a more satisfactory test of progress, being found in accustoming the student to take part in his own education." Or, again, "the student is regarded, not as a receptacle for information, but *as a possible producer of independent thought*." The attempt is made "not merely to offer a series of special courses, each of adequate thoroughness, but to keep up, as far as possible, a parallelism of treatment and to co-ordinate these parallel courses into a larger whole." To such endeavours we can merely wish the most ample success.

We trust, however, that the "humanities" will not be allowed to encroach too far on the time and attention of the school, as they have a tendency to do in Britain. We have great confidence in the guidance of Professor Geddes.

*Incandescence Lamps.* Price List. The Edison and Swan United Electric Light Company, Limited, Section I.

*Electric Light Installation Fittings.* Price List. The Edison and Swan United Electric Light Company, Limited. Section II.

*Electric Light Measuring Instruments.* The Edison and Swan United Electric Light Company, Limited. Section III.

These copious illustrated price lists will be exceedingly useful for municipal authorities who may be contemplating the introduction, extension, or improvement of an electric light installation.

It is to be hoped that the instruments used for measuring electric current as supplied to consumers will prove in practice more trustworthy than the gas-meter, which has earned for itself the unenviable name of the "mechanical Ananias."

## CORRESPONDENCE.

### OXIDATION PRODUCTS OF GLUCOSE.

*To the Editor of the Chemical News.*

Sir,—Will any of your readers kindly inform me of the oxidation products of glucose when treated with Fehling's solution? The text-books on analysis (Sutton, Blyth, &c.) are satisfied with the statement that $Cu_2O$ is formed by reduction and overlook the rest of the reaction. It certainly seems surprising that the chemistry of so important a process should receive so little attention.—I am, &c.,

A. C. Langmuir.

School of Mines, Columbia College,
New York.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 15, April 10, 1893.

**Volatility of Manganese.**—S. Jordan.—The author's former researches have been confirmed by H. H. Lorenz and Heusler, who conclude that manganese, unlike nickel and iron, does not react with carbon monoxide, and that it is volatilised as a metal, at little above its point of fusion.

**Determination of Atomic Weights by the Method of Limit.**—G. Hinrichs.—The author finds that for each atom of the unique and primitive matter contained in hydrogen there are exactly sixteen in the atom of oxygen.

**Nitro-Copper.**—Paul Sabatier and J. R. Senderens.—This compound is obtained by reducing cupric oxide and directing upon the metal thus procured, at 25° or 30°, vapours of nitrogen peroxide. The compound may be represented by the formula $Cu_2NO_2$. It is stable in dry air in the cold, but it is decomposed by temperatures exceeding 90°. It reacts violently with water.

**Isomerism of the Amido-Benzoïc Acids.**—Oechsner de Coninck.—The author has pursued the comparative study of the three amido-benzoïc acids, determining their solubility in neutral solvents such as pure alcohol and ether, methylic alcohol, acetone, methyl and ethyl iodides, chloroform, bromoform, oil of turpentine, and distilled water at different temperatures.

**Phthalocyanacetic Ether.**—P. Th. Müller.—This paper does not admit of useful abridgment.

**Observations on a Series of Novel Forms of Snow, collected at very Low Temperatures.**—Gustav Nordenskiöld.—These snow-flakes seem a connecting-link between the geometrical forms of dead nature, bounded by plane surfaces and the curved and rounded forms of organised beings.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 2, 1893.

**Simple Separation of Iron and Alumina.**—H. Bornträger.—Both hydroxides are precipitated together, ignited, and weighed as oxides. They are then re-dissolved in hydrochloric acid, rendered almost neutral with potassa-lye—not soda—and both oxides are then precipitated with neutral liquid potash soap, as sold by A. Keysser, of Hanover, or A. Gude, of Leipzig. The precipitation must be effected in heat, and an excess of soap must in any case be avoided, as the oleates are otherwise re-dissolved. It is filtered through a filter moistened with hot water, and washed with hot water until the potassium chloride is removed. The filter is then partially dried over calcium chloride until the bulk of the water is removed. The gelatinous mass is then treated with hot petroleum until it runs off colourless, and consequently all iron oleate has passed into solution. The filter is burnt, and the residual porous snow-white alumina is weighed. As a precaution, the petroleum solution may be burnt and incinerated so as to weigh the iron oxide. Ferrous oxide may be separated from alumina in this manner without previous oxidation.

**Rapid Reduction of Potassium Platinum Chloride.**—H. Bornträger.—The compound is dissolved in boiling water, and the platinum is precipitated by liquid potash soap. It falls to the bottom as a smeary and sandy light-coloured clot. The supernatant solution is decanted off, and the clot (which consists of a double salt of potassium chloride and platinum oleate), is ignited in a porcelain crucible. Thus, in a few minutes we obtain a very effective platinum-black, which is freed from potassium chloride by washing with hot water. The clot, on ignition, leaves 42 per cent residue with 23 per cent platinum.

**Separation of Strontium and Calcium.**—Prof. R. Fresenius.—The author, as the final result of his prolonged investigations, concludes that only the method of H. Rose, as improved by F. Stromeyer, can be recommended for a true separation.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 86.

**Use of the Safety-Lamp for the Detection of Inflammable Vapours.** — Frank Clowes.—(From the Chemical News).

## MISCELLANEOUS.

**The Institute of Chemistry of Great Britain and Ireland.**—An Extraordinary General Meeting was held at 30, Bloomsbury Square, London, W.C., on Thursday, the 27th April, 1893, for the following purposes, viz.:—I.—To pass the following resolution: "That the Council be empowered to expend a sum not exceeding £1000 upon the erection of a building to be used as a laboratory, upon the ground at the back of the house at 30, Bloomsbury Square." II.—To consider the Report of the Censors, and pass a resolution, or resolutions, thereon.

*Report of the Censors.*—"The Censors having received information which tends to show that practices of an unprofessional character are unduly prevalent among practising analytical chemists, desire to draw the attention of the Council to the necessity for establishing among the members of the Institute more definitely than at present a standard of conduct in a professional sense comparable with that which is recognised in the professions of law and medicine. They therefore recommend that at the next conference, which should be summoned as an extraordinary general meeting in accordance with Bye-law 5, the following resolutions shall be submitted: I.—That the following acts or any of them shall be held to be 'discreditable to the profession of analytical and consulting chemist,' viz.: (1) Advertising for practice in newspapers, journals, magazines, or other published papers. (2) Sending out by post or otherwise letters, circulars, or cards, offering professional services. (3) Undertaking through another person or agency the performance of professional work at fees representing only a small fraction of the usual recognised scale of fees for analytical work. (4) Supplying to other persons, not being qualified chemists, reports upon samples or processes with the knowledge that these other persons will issue such reports as their own work. (5) Issuing or allowing to be issued certificates of purity or superiority concerning advertised commodities, such certificates being either not based upon the results of an analysis, or containing exaggerated, irrelevant, or merely laudatory expressions, designed to serve the purposes of a trade puff. (6) The unauthorised use of letters indicating University degrees. II.—That in the opinion of this meeting the Council will be justified in regarding these acts as offences of the kind referred to in the Charter (chap. 16, 3) as discreditable to the profession of analytical and consulting chemist.—Signed this First day of December, 1892, William A. Tilden (*Chairman*), J. Bell, Charles E. Cassal, E. Frankland, T. E. Thorpe (Censors)."

**Smithsonian Institution. — Circular Concerning the Hodgkins Fund Prizes.** — In October, 1891, Thomas George Hodgkins, Esq., of Setauket, New York, made a donation to the Smithsonian Institution, the income from a part of which was to be devoted "to the increase and diffusion of more exact knowledge in regard to the nature and properties of atmospheric air in connection with the welfare of man." With the intent of furthering the donor's wishes, the Smithsonian Institution now announces the following prizes to be awarded on or after July 1, 1894, should satisfactory papers be offered in competition:—

1. A prize of 10,000 dollars for a treatise embodying some new and important discovery in regard to the nature or properties of atmospheric air. These properties may be considered in their bearing upon any or all of the sciences,—*e.g.*, not only in regard to Meteorology, but in connection with hygiene, or with any department whatever of biological or physical knowledge.

2. A prize of 2000 dollars for the most satisfactory essay upon: (*a*) The known properties of atmospheric air considered in their relationships to research in every department of natural science, and the importance of a study of the atmosphere considered in view of these relationships. (*b*) The proper direction of future research in connection with the imperfections of our knowledge of atmospheric air, and of the connections of that knowledge with other sciences. The essay as a whole should tend to indicate the path best calculated to lead to worthy results in connection with the future administration of the Hodgkins foundation.

3. A prize of 1000 dollars for the best popular treatise upon atmospheric air, its properties and relationships (including those to hygiene, physical and mental). This essay need not exceed 20,000 words in length; it should be written in simple language, and be suitable for publication for popular instruction.

4. A medal will be established, under the name of the Hodgkins Medal of the Smithsonian Institution, which will be awarded annually or biennially, for important contributions to our knowledge of the nature and properties of atmospheric air, or for practical applications of our existing knowledge of them to the welfare of mankind. This medal will be of gold, and will be accompanied by a duplicate impression in silver or bronze.

The treatises may be written in English, French, German, or Italian, and should be sent to the Secretary of the Smithsonian Institution, Washington, before July 1, 1894, except those in competition for the first prize, the sending of which may be delayed until December 31, 1894. The papers will be examined, and prizes awarded, by a committee to be appointed as follows:—One member by the Secretary of the Smithsonian Institution, one member by the President of the National Academy of Sciences, one by the President, pro tem., of the American Association for the Advancement of Science; and the committee will act, together with the Secretary of the Smithsonian Institution as member, ex officio. The right is reserved to award no prize if, in the judgment of the committee, no contribution is offered of sufficient merit to warrant an award. An advisory committee of not more than three European men of science may be added at the discretion of the Committee of Award. If no disposition be made of the first prize at the time now announced, the Institution may continue it until a later date, should it be made evident that important investigations relative to its object are in progress, the results of which it is intended to offer in competition for the prize. The Smithsonian Institution reserves the right to limit or modify the conditions for this prize after December 1, 1894, should it be found necessary. Should any of the minor prizes not be awarded to papers sent in before July 1, 1894, the said prizes will be withdrawn from competition. A principal motive for offering these prizes is to call attention to the Hodgkins Fund, and the purposes for which it exists, and accordingly this circular is sent to the principal universities, and to all learned societies known to the Institution, as well as to representative men of science in every nation. Suggestions and recommendations in regard to the most effective application of this fund are invited. It is probable that special grants of money may be made to specialists engaged in original investigation upon atmospheric air and its properties. Applications for grants of this nature should have the indorsement of some recognised academy of sciences, or other institution of learning, and should be accompanied by evidences of the capacity of the applicant, in the form of at least one memoir already published by him, based upon original investigation. To prevent misapprehension of the founder's wishes, it is repeated that the discoveries or applications proper to be brought to the consideration of the Committee of Award, may be in the field of any science or any art without restriction, provided only that they have to do with "the nature and properties of atmospheric air in connection with the welfare of man." Information of any kind desired by persons intending to become competitors will be furnished on application. All communications in regard to the Hodgkins Fund, the Hodgkins Prizes, the Hodgkins Medal, and the Hodgkins Fund Publications, or applications for grants of money, should be addressed to S. P. Langley, Secretary of the Smithsonian Institution, Washington, U.S.A.—S. P. Langley, Secretary of the Smithsonian Institution, Washington, March 31, 1893.

## MEETINGS FOR THE WEEK.

Monday, May 1st.—Medical, 8.30. (Annual Oration).
— Society of Arts, 8. "Some Masters of Ornament," by Lewis Foreman Day. (Cantor Lectures).
— Society of Chemical Industry, 8. "The Gasification of Coal and of Liquid Hydrocarbons," by Dr. P. Dvorkovitch. "Estimation of Tannic and Gallic Acids," by W. P. Dreaper.
— Royal Institution, 5. (Annual Meeting).

Tuesday, 2nd.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "Modern Society in Chine," by Prof. R. K. Douglas.
— Society of Arts, 8. "Russian Industrial Art," by E. Delmar Morgan.

Wednesday, 3rd.—Society of Arts, 8. "Practical Electrical Problems at Chicago," by Prof. Silvanus P. Thompson, F.R.S.

Thursday, 4th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
— Chemical, 8. Ballot for the Election of Fellows. "Hydrates of Potassium, Sodium, and Lithium Hydroxides," by S. U. Pickering, F.R.S. "Notes on Marsh's and Reinsch's Tests for Arsenic," by J. Clark, Ph.D. "The Formation of Hydrogen Peroxide in Organic Liquids," by A. Richardson, Ph.D. "The Supposed Saponification of Linseed Oil by White-lead," by J. B. Hannay and A. E. Leighton. "Notes on the Capillary Separation of Substances in Solution," by L. Reed.

Friday, 5th.—Royal Institution, 9. "Fogs, Clouds, and Lightning," by Shelford Bidwell, F.R.S.
— Geologists' Association, 8.
— Quekett Club, 8.
— Chemical Society, 8. Hoffman Memorial Meeting. Addresses by the Right Hon. Lord Playfair, Sir F. A. Abel, F.R.S., and W.H. Perkin, F.R.S.

Saturday, 6th.—Royal Institution, 3. "Johnson and Milton," by Henry Craik, LL.D.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1745.

# ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.[*]

By W. LAPRAIK, Ph.D., F.I.C.

In the following research the optical properties of a series of chromium salts have been investigated, which, in part, are recorded for the first time. I referred to the literature on the subject,[†] but more particularly to that relating to chromium oxalate. The main objects of this research were as follows:—

1. To show the spectroscopic relation existing between the complex salts of oxalic acid and chromium, and other metals chemically related to chromium.
2. To determine if similar salts were produced with acids chemically homologous with oxalic acid, and if such existed to determine their spectroscopic relations.
3. To determine if any spectroscopic relation existed between the compounds formed when chromium hydroxide was dissolved in various organic acids, and the known chemical composition of such acids.

### *Apparatus and Method Employed.*

For the examination of the absorption-spectra of the compounds mentioned in this research, I used a single prism spectroscope constructed by Browning. The prism was of extra dense flint-glass, having a refractive surface of 10·9 square c.m. The collimator and telescope lenses were 30 m.m. in diameter. The length of focus of collimator and telescope being 33 c.m., while the magnification of the telescope was 10 diameters. The circle was divided into thirds of a degree, and the vernier was divided into 20 divisions, thus enabling one to read easily to minutes. All readings were made with the assistance of a lens. The slit was fitted with a right-angled prism so that two spectra could be superposed. In some experiments—mentioned in the text—two prisms were used, but the dispersion was then too great, with the result that the faint absorption-bands were all but invisible; also in other cases a very fine ruled grating was substituted with a like result.

### *The Light Source.*

It is important in work of this character to have a source of light as constant as possible, and at the same time of sufficient illuminating power. With this idea in view a quick-combustion petroleum-lamp, having a circular wick, was used. This gave a very powerful white light, having an illuminating power of 48 candles (English). In some cases the electric light, and also sun light reflected from a heliostat, were used, but the absorption-spectra given did not differ in any material way from those given by the foregoing arrangement.

The containing vessels for the solutions under examination were similar to those described by Hansen.[‡] They were plate glass troughs, each consisting of two faces, which were perfectly parallel, and another centre-piece, also of plate glass, hollowed out. The three parts were held together by a cement formed by a hot aqueous solution of isinglass. These troughs had a capacity of 3 to 5 c.c. When a slightly increased thickness in the layer of the solution was required, two or more troughs could be placed one in front of the other, and held together by an indiarubber band. When greater thicknesses were required, as 15 c.m., then glass tubes were used, having their ends ground and fitted with glass plates.

### *The Determination of Wave-Lengths for the Different Parts of the Scale.*

This was accomplished by means of graphical interpolation (Wiedemann-Ebert, *Practicum*, p. 295). The numbers in the following table were observed; under λ are the wave-lengths, and under *a* are angular measurements from the scale.

| | λ. | *a*. |
|---|---|---|
| Kα.. .. .. .. | 770·0 | 34° 25′ |
| | 720·0 | 34° 36′ |
| B .. .. .. .. | 686·7 | 34° 46′ |
| Liα.. .. .. .. | 670·5 | 34° 52′ |
| | 662·5 | 34° 56′ |
| C .. .. .. .. | 656·2 | 34° 58′ |
| D .. .. .. .. | 589·2 | 35° 30′ |
| | 558·0 | 35° 50′ |
| | 531·5 | 36° 9′ |
| E .. .. .. .. | 526·9 | 36° 14′ |
| | 491·5 | 36° 45′ |
| F .. .. .. .. | 486,0 | 36° 53′ |
| | 477·0 | 37° 5′ |
| Sr .. .. .. .. | 361·0 | 37° 27′ |
| | 447·5 | 37° 48′ |
| | 435·0 | 38° 11′ |
| G .. .. .. .. | 430·7 | 38° 16′ |
| | 425·0 | 38° 29′ |
| | 415·5 | 38° 46′ |
| Kβ .. .. .. .. | 404·0 | 39° 12′ |
| H .. .. .. .. | 396·8 | 39° 27′ |

The results are tabulated in an accompanying table.[*] The measurements are in wave-lengths. Continuous absorption is shown in the first and last columns, and the absorption-bands in the columns numbered 1, 2, 3, 4, 5. Each spectra given is numbered at the side, and when referred to in the text the number of the spectrum is placed in parentheses. Two numbers separated by a short vertical line (*e.g.*, spectrum 4) indicate two separate absorption-bands.

### *Experiments and Resulting Observations.*

*Potassium Chromoxalate*, $K_6Cr_2 6C_2O_4+6H_2O$ (1 and 2)—This salt was obtained by the method first proposed by Gregory and modified by Croft, viz., by the action of 19 parts of potassium dichromate on a mixture of a saturated hot solution of 23 parts of potassium oxalate and 55 parts of crystallised oxalic acid; when the action had ceased the solution was evaporated to dryness, re-dissolved in water, and crystallised in a flat-bottomed dish, to which the crystals firmly adhered, and thus could be easily examined by transmitted light. It was found that in some cases the crystals were laid down on different axes, so that some appeared red while others were of the well-known corn-flower blue colour. That the crystals were homogeneous was easily seen on re-solution and re-crystallisation, when no red crystals, but blue ones, were obtained; and, further, on rotating the red-coloured crystals they transmitted blue rays, for they are doubly refractive. The blue light transmitted by the crystals (1) gave continuous absorption to 800; then a thin faint band at 717, then a very dark and sharp band 710—704. Accompanying this are two fainter bands, the centres of which are 683 and 663 respectively; then a broad absorption from 660—518, and lastly continuous absorption from 434. The red light transmitted by the other axes of the crystal could not be so easily examined; the thin, dark,

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[*] *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

[†] *Jahresb.*, vii., 392, (1854); Brewster, *Phil. Mag.*, vi., 305 (1835); Brewster, *Phil. Mag.*, vii., 436 (1835); W. Haidinger, "Ueber den Pleochroismus des oxalsauren Chromoxydkalis," *Pogg. Ann.*, lxxvi., 107 (1849); J. Müller, "Ueber die natürlichen Farben durchsichtiger Körper," *Pogg. Ann.*, lxxix., 347 (1850); Grailich, "Krystallographische optische Untersuchungen," *Wien*, 146 (1858); Th. Erhard, "Untersuchungen über die Absorption des Lichtes in einigen Chromsalzen," Inaug.-Dissertat., Leipzig, 1875; E. Wiedemann, *Wied. Ann.*, v., 515 (1878); Croft, "Ueber ein neues Oxalat des Kaliumchromats," *Phil. Mag.*, xxi., 197 (1842).

[‡] Hansen, "Die Farbstoffe des Chlorophylls." Darmstaat, 1889.

[*] In the original memoir there is given a map of the absorption-spectra.

sharp band was seen, but its position could not be measured; but the broad absorption was continuous from 650, the whole of the green and blue of the spectrum being absorbed.

A saturated solution of the salt was now examined. The absorption-spectrum was similar in kind to that given by the blue crystal, all the bands in the one being represented in the other; but their positions in the spectrum are not identical, the bands in the aqueous solution being moved slightly nearer the blue end of the spectrum. The measurements are continuous absorption to 820; a faint band at 710, a strong sharp band at 704—698, a faint band at 681, another faint band at 663; then broad absorption from 642 to 508, and continuous absorption from 474. It will thus be seen that all the bands in the solution are slightly nearer the blue end of the spectrum, excepting in the case of 663, which is faint and difficult to measure.

### *Other Chromoxalates.*

It was thought expedient to prepare some other salts analogous to the above, in which the potassium is wholly or in part replaced by other metals, and to determine how their absorption-spectra differed.

*Silver Chromoxalate*, $Ag_6Cr_26C_2O_4+Aq$.—This salt is easily made by decomposing the corresponding potassium salt with an equivalent of silver nitrate. The silver salt easily separates by spontaneous evaporation in minute highly coloured crystals. These were, however, too small and opaque to see through, so that their absorption-spectrum could not be examined. An aqueous solution of the salt was made, and this gave an absorption-spectrum identical with that given by the corresponding potassium salt.

*Barium Chromoxalate*, $Ba_3Cr_26C_2O_4+Aq$.—This salt is not very soluble in cold water, but by using a considerable thickness of a hot solution, the absorption-spectrum was again found to be the same as that given by the potassium salt.

Now a compound having the composition—

$$K_2Ca_2Cr_26C_2O_4+8H_2O,$$

which had been prepared and described by Hartley (*Proc. Roy. Soc.*, xxi., 499) was used. I prepared a hot concentrated solution of this body, and I found as in the previous cases no difference in the absorption-spectrum of this salt and that of the corresponding compound of potassium chromoxalate.

It was now thought to be of some interest to prepare if possible a salt in which part of the potassium in potassium chromoxalate was replaced by ammonium,

$$K_3(NH_4)_3Cr_26C_2O_4+5H_2O.$$

For this purpose a hot saturated solution containing 29·5 grms. of potassium dichromate was added to one containing 28·4 grms. crystallised ammonium oxalate and 88·2 grms. crystallised oxalic acid.* After the action had ceased the solution was evaporated to small bulk, and it was then observed that free ammonia escaped with the steam. After standing, a crop of beautifully formed prismatic crystals was obtained which were not distinguishable in appearance from potassium chromoxalate, only that the crystals are usually smaller in size. They also exhibit the well-known corn-flower blue colour when examined by transmitted light. The salt was now subjected to analysis. The analysis of this and analogous salts is surrounded with unusual difficulties.

The ammonia was determined by heating a known weight with a solution of caustic potash and passing the evolved ammonia into standard acid. For the determination of chromium the salt was first carefully decomposed by heat, and then the residue was fused with about three parts its weight of a mixture of sodium carbonate and potassium nitrate. After fusion the mass was dissolved in water and acidified with hydrochloric acid, reduced by sulphurous acid, and then precipitated by ammonia solution. The precipitated chromium hydroxide was washed and re-dissolved in hydrochloric acid, and then re-precipitated. This was repeated in all cases at least twice. In some cases the estimation of the chromium was attempted by precipitation as mercurous chromate, using for this purpose mercurous nitrate, while the solution had been previously acidulated by nitric acid, but the alkaline chromate frequently became reduced, and consequently the results were unreliable, and they were therefore discarded. The potassium was estimated as chloride.

The following are the numbers obtained:—

| Grm. | | | Grm. | Per cent. |
|---|---|---|---|---|
| 0·9567 | lost at | 100° | 0·0947 | = 9·89 $H_2O$. |
| 0·5819 | ,, | ,, | 0·0577 | = 9·91 $H_2O$. |
| 0·8992 | gave | ,, | 0·0510 $NH_3$ | = 6·00 $NH_4$. |
| 0·5819 | ,, | ,, | 0·1420 KCl | = 12·77 K. |
| 1·6010 | ,, | ,, | 0·2750 $Cr_2O_3$ | = 11·78 Cr. |
| 1·1935 | ,, | ,, | 0·2042 $Cr_2O_3$ | = 11·74 Cr. |
| 0·7304 | ,, | ,, | 0·1240 $Cr_2O_3$ | = 11·55 Cr. |

| | $K_3(NH_4)_3Cr_26C_2O_4+5H_2O$. Calculated. | Found. | | |
|---|---|---|---|---|
| $H_2O$ .. .. | 10·07 | 9·89 | 9·91 | — |
| $NH_4$ .. .. | 6·04 | 6·00 | — | — |
| K .. .. .. | 13·10 | 12·77 | — | — |
| Cr . .. .. | 11·69 | 11·78 | 11·74 | 11·55 |

The spectrum of the light transmitted by the crystals of this salt was examined, and again it was found to be identical with the absorption-spectrum given by the crystals of potassium chromoxalate. The salt is easily soluble in water, and it was found that the absorption-spectrum given by this solution was also exactly the same as that given by a solution of potassium chromoxalate. It follows, therefore, that there exist the same relation between the absorption-spectra given by the crystal and by the aqueous solution of both of these salts; that is, that the more important absorption-bands in the case of the crystal are nearer the red end of the spectrum than is the case when either salt is dissolved in water. From the fact* that all these salts give identical spectra when examined under similar conditions, that these bodies do not behave chemically as simple oxalates, and that the potassium of potassium chromoxalate can be replaced either wholly or in part by other metals, it is clear that we are dealing with very stable combinations, such combination, however, being not of the ordinary character of double salts, but more nearly approaching in character bodies like the double cyanides, as, for example, potassium ferricyanide, $K_6Fe_2(CN)_{12}$. If such be the case, the chromium in such salts would play the part of part of the acid radicle; and as the acid $H_6Fe_2(CN)_{12}$ exists, it does not seem improbable but that a body of the composition $H_6Cr_26C_2O_4$ may also exist. The first step in this direction was to prepare chromium oxalate and to study its properties.

### *Chromium Oxalate* (3 and 4).

It is well known that chromium hydroxide is soluble in oxalic acid, but there is great difficulty in isolating the oxalate itself.† Graham says ("Graham's Researches," p. 376):—"I made several attempts to crystallise chromium oxalate but without result, so I had no opportunity of studying its constitution in relation to the above" (*i.e.*, potassium chromoxalate).

Two experiments were made. In the first, 113·4 grms. re-crystallised oxalic acid were dissolved in hot water, and to this was added 20 grms. of chromium trioxide (free from sulphuric acid), dissolved in water,—these propor-

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* These quantities are those required for the compound—$K_2(NH_4)_4Cr_26C_2O_4$.

* See also B. O. Peirce and E. Wiedemann, *Wied. Ann.*, v., 515 (1878).

† See also Kistiakowsky, *Zeit. f. Phys. Chem.*, vi., 97 (1890).

tions being those indicated by theory for the preparation of the compound $H_6Cr_26C_2O_4$. After effervescence had ceased, the solution was evaporated to small bulk; in the meantime it changed colour, but finally became light blue by daylight but purple by lamplight. It was put aside to crystallise over sulphuric acid; oxalic acid separated, which was removed from time to time until a thick treacle-like mass remained, which was finally obtained in a semi-crystalline state, and having a dark red colour.

In the second experiment proportionately less oxalic acid was used. The quantities taken were 132 grms. re-crystallised oxalic acid and 30 grms. chromium trioxide (free from sulphuric acid); they were dissolved in water, and treated in the same manner as in the last experiment. The final colour of the solution was also the same. The slight excess of oxalic acid readily crystallised out, and it was removed leaving a thick treacle-like mass as in the last experiment, which finally crystallised. The salt was analysed with the following result:—

| Grm. | | Grm. | Per cent. |
|---|---|---|---|
| 1·0173 | lost at 120° | 0·2310 | = 22·61 $H_2O$. |
| 0·9484 | ,, ,, | 0·2130 | = 22·46 $H_2O$. |
| 0·3992 | gave ,, | 0·1265 $Cr_2O_3$ | = 31·69 $Cr_2O_3$. |
| 0·7615 | ,, ,, | 0·3510 $C_2O_3$ | = 46·09 $C_2O_3$. |
| 0·8520 | ,, ,, | 0·3700 $C_2O_3$ | = 45·95 $C_2O_3$. |

| | $Cr_23C_2O_4+6H_2O$. Calculated. | Found. | |
|---|---|---|---|
| $Cr_2O_3$ .. .. | 31·99 | 31·69 | — |
| $C_2O_3$ .. .. | 45·34 | 45·95 | 46·09 |
| $H_2O$ .. .. | 22·67 | 22·61 | 22·46 |

The $C_2O_3$ was determined by Graham's method, viz., by heating the salt with concentrated sulphuric acid and noting the loss due to $CO_2$ and CO.

The salt, hydrated chromium oxalate, when seen in mass is nearly black, but in thin layers it is reddish-blue. It is very soluble in water, the solution being reddish-blue by lamplight. It is deliquescent. It is soluble in ordinary alcohol, but the anhydrous salt does not appear to be soluble in dry alcohol. The anhydrous salt is obtained by heating the hydrated salt to 120° C.; it has a fine deep green colour. Curiously enough it does not appear to be immediately soluble in cold water; after standing some time, however, it becomes hydrated and then dissolves. In hot water it is instantly soluble. It gives no precipitate with calcium chloride or with silver nitrate solutions, as complex salts are thus formed. Sodium carbonate solution does not yield a precipitate in the cold, but the solution becomes green, and on boiling is precipitated. Potassium bicarbonate both in solution and in the solid state produces a vigorous effervescence. A very thin layer of a saturated solution of the salt dissolved in water gave the following absorption spectrum (3).

Continuous absorption ending about 714. Then a rather broad, somewhat indefinite band from 704—689. Then a shadow at 653 joining the broad absorption from 610—503. Then some blue light transmitted, and finally continuous absorption from 471.

It is to be observed that the absorption-spectrum of a solution of chromium oxalate is not the same as that given by the chromoxalates under the same conditions. The dominant band is much broader and less distinct in the case of chromium oxalate; its edges are blunter, and gradually merge into the lighter part of the spectrum. They both begin at the same point, 704, but in no other respect do they resemble one another. Altering the thickness of the layer of solution under examination does not bring out any further similarity, and lastly, the three fainter bands in the chromoxalates are entirely absent in chromium oxalate. The absorption-spectrum of the chromoxalates then is not that of chromium oxalate; in other words, the absorption-spectrum of the chromoxalates is not entirely due to the vibrations of *part* of the molecule, but to the vibrations of the whole combination; and as far as these experiments go, it seems that the more positive part of the combination has no influence in damping the molecular vibrations.

A solution of chromium oxalate was made by digesting an *excess* of chromium hydroxide in a concentrated aqueous solution of oxalic acid. The filtered solution gave exactly the same spectrum as the foregoing. The same remark applies to the absorption-spectrum given by the alcoholic solution of hydrated chromium oxalate.

The solid chromium oxalate is somewhat difficult to examine for its absorption spectrum, but by evaporation of a solution of the salt on a glass slide I was able to see that the dominant band appeared to be slightly nearer the red end of the spectrum than was the case in the solution. Although no compound of chromium oxalate and oxalic acid crystallises on evaporation of a solution containing these substances, yet there is reason for believing that there are two such compounds which exist in solution.

It was observed that if chromium oxalate be dissolved in water, and then some oxalic acid added, and if the solution be gently warmed, an absorption-spectrum is obtained giving two sharp, dark, thin bands in the red part of the spectrum, and the three fainter incidental bands as well, which is so characteristic of the chromoxalates, but which are not given by chromium oxalate itself. The significance of this two-lined spectrum will be again referred to under the red potassium chromoxalate. The absorption-spectrum (4) is as follows.

Continuous absorption ending about 800. Then a faint band at 710. A sharp, thin, very dark band, the centre of which is 704. A somewhat fainter but equally sharp band, its centre being 695. Then the two other incidental bands at 681 and 663, respectively. The broad absorption at 650—505, and continuous absorption from 471.

By prolonged heating of this solution, and if necessary a further addition of oxalic acid, the band at 695 fades out, and finally disappears altogether, and there remains an absorption-spectrum agreeing in all particulars with that given by the chromoxalates, and that in a solution originally containing only chromium oxalate and oxalic acid.

It has been shown that the chromoxalates of the metals give identical absorption-spectra; one should, therefore, expect that the compound hydrogen chromoxalate would also give the same absorption-spectrum. Therefore, I think one is forced to the conclusion that it is this compound, hydrogen chromoxalate, which gives an absorption-spectrum agreeing in all points with that given by other chromoxalates. Although I have not succeeded in isolating this body yet, there are strong reasons given above for believing in its existence.

(To be continued).

# THE CHEMICAL CONSTITUTION OF THE ATMOSPHERE, AND ITS BEARING ON GEOLOGICAL CHANGES.

By JAMES MORRIS.

In the Chemical News, vol. lxvii., p. 135, there is an article by Dr. Phipson, in which he expressed some of his own views, and also partly quotes those of the late Prof. Koene. At p. 309 of the preceding volume I described my experiments on the mineralisation of alumina, carbonic acid being the agent used. I spoke of the experiments of Sir James Hall, and more particularly of Doelter's modification of these experiments. The latter mineralogist found that when a plentiful supply of carbonic acid was present, the mineralisation occurred without pressure. This latter factor in geological change may in some cases have been overrated, and perhaps such considerations have tended to retard attempts at the synthesis of minerals.

In considering the factor of pressure in geology, a distinction must be made between the constant pressure caused by superincumbent mass, and the variable, and in some cases temporary, pressure caused by expansion and contraction. Minerals deep down in the earth are sometimes mechanically protected from pressure of the former kind. In any case the results of Doelter's experiments are noteworthy.

From the presence of combustible substances in the primitive rocks, from the enormous leaves of the plants which formed the coal-flora, from beings capable of existing without free oxygen, and from the higher excitability of modern man, the general opinion expressed in Dr. Phipson's article is that the amount of carbonic acid in the atmosphere has gradually diminished, and that of free oxygen increased.

In most cases the available evidence in the inorganic world is more direct and measurable than that in the organic. In certain phases of geological evidence, however, the case is reversed. Thus, the petrified remains of a tree, or of a crab, give us a veritable stone picture of the plant or animal, often with great perfection of detail. What various metamorphoses many minerals may have undergone is neither measurable nor imaginable.

Koene's doctrine, the starting-point of which is that the atmosphere in earlier geological ages consisted of nitrogen, carbonic acid, and vapour of water, may yet come to receive some confirmation from the still somewhat neglected science of mineral synthesis.

Regard must be had to the temperature of dissociation of the carbonic acid and the water vapour, compared with that of the solidification of the earth's crust. Perhaps we may at least assume that many mineralogical transformations took place during the cooling of the crust at a period when the atmosphere still contained a large proportion of carbonic acid. The enormous quantity of this gas still evolved in volcanic regions is perhaps the residue of a vastly greater proportion present in earlier times. The presence of carbonic acid and carbonic oxide in meteorites should not be overlooked.

The remarks already made may suggest some thoughts in regard to the interdependence of the sciences.

217, West George Street, Glasgow,
April, 1893.

## MAGNETIC PROPERTIES OF LIQUID OXYGEN.*

By Prof. DEWAR, M.A., LL.D., F.R.S.

After alluding to the generous aid which he had received both from the Royal Institution and from others in connection with his researches on the properties of liquid oxygen, and to the untiring assistance rendered him by his co-workers in the laboratory, Prof. Dewar said that on the occasion of the commemoration of the centenary of the birth of Michael Faraday he had demonstrated some of the properties of liquid oxygen. He hoped that evening to go several steps further, and to show liquid air, and to render visible some of its more extraordinary properties.

The apparatus employed consisted of the gas-engine downstairs, which was driving two compressors. The chamber containing the oxygen to be liquefied was surrounded by two circuits, one traversed by ethylene, the other by nitrous oxide. Some liquid ethylene was admitted to the chamber belonging to its circuit, and there evaporated. It was then returned to the compressor as gas, and liquefied, and thence again into the chamber as required. A similar cycle of operations was carried out with the nitrous oxide. There was a hundredweight of liquid ethylene prepared for the experiment. Ethylene was obtained from alcohol by the action of strong sulphuric acid. Its manufacture was exceedingly difficult, because dangerous, and as the efficiency of the process only amounted to 15 or 20 per cent, the preparation of a hundredweight of liquid was no light task. The cycle of operations, which for want of time was not fully explained, was the same as that commonly employed in refrigerating machinery working with ether or ammonia.

The lecturer then exhibited to the audience a pint of liquid oxygen, which by its cloudy appearance showed that it contained traces of impurity. The oxygen was filtered, and then appeared as a clear transparent liquid with a slightly blue tinge. The density of oxygen gas at −182° C. is normal, and the latent heat of volatilisation of the liquid is about 80 units. The capillarity of liquid oxygen at its boiling-point was about one-sixth that of water. The temperature of liquid oxygen at atmospheric pressure, determined by the specific heat method, using platinum and silver, was −180° C.

Reference was then made to a remarkable experimental corroboration of the correctness for exceedingly low temperatures of Lord Kelvin and Prof. Tait's thermo-electric diagram. If the lines of copper and platinum were prolonged in the direction of negative temperature, they would intersect at −95° C. Similarly, the copper and palladium lines would cut one another at −170° C. Now if this diagram were correct, the E.M.F. of the thermo-electric junctions of these two pairs of metals should reverse at these points. A Cu−Pt junction connected to a reflecting galvanometer was then placed in oxygen vapour and cooled down. At −100° C. the spot of light stopped and reversed. A Cu−Pd junction was afterwards placed in a tube containing liquid oxygen, and a similar reversal took place at about −170° C.

Liquid oxygen is a non-conductor of electricity; a spark, taken from an injunction coil one m.m. long, in the liquid requires a potential equal to a striking distance in air of 25 m.m. It gave a flash now and then, when a bubble of the oxygen vapour in the boiling liquid came between the terminals. Thus liquid oxygen is a high insulator. When the spark is taken from a Wimshurst machine the oxygen appears to allow the passage of a discharge to take place with much greater ease. The spectrum of the spark taken in the liquid is a continuous one, showing all the absorption-bands.

As to its absorption-spectrum, the lines A and B of the solar spectrum are due to oxygen, and they came out strongly when the liquid was interposed in the path of the rays from the electric lamp. Both the liquid and the highly compressed gas show a series of five absorption-bands, situated respectively in the orange, yellow, green, and blue of the spectrum.

Experiments prove that gaseous and liquid oxygen have substantially the same absorption-spectrum. This is a very noteworthy conclusion considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen. The persistency of the absorption through the stages of gaseous condensation towards complete liquidity, implies a persistency of molecular constitution which we should hardly have expected. The absorptions of the class to which A and B belong must be those most easily assumed by the diatomic molecules $(O_2)$ of ordinary oxygen; whereas the diffuse bands above referred to, seeing they have intensities proportional to the square of the density of the gas, must depend on a change produced by compression. This may be brought about in two ways, either by the formation of more complex molecules, or by the constraint to which the molecules are subjected during their encounters with one another.

When the evaporation of liquid oxygen is accelerated by the action of a high expansion-pump and an open test-tube is inserted into it, the tube begins to fill up with liquid atmospheric air, produced at the ordinary barometric pressure.

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* Abstract of a Lecture delivered at the Royal Institution of Great Britain, Friday, June 10, 1892.

Dr. Janssen had recently been making prolonged and careful experiments on Mont Blanc, and he found that these oxygen lines disappeared more and more from the solar spectrum as he reached higher altitudes. The lines at all elevations come out more strongly when the sun is low, because the rays then have to traverse greater thicknesses of the earth's atmosphere.

Michael Faraday's experiments made in 1849 on the action of magnetism on gases opened up a new field of investigation. The following table, in which + means "magnetic" and – means "negative," summarises the results of Faraday's experiments.

*Magnetic Relations of Gases (Faraday).*

| | In air. | In carbonic acid. | In hydrogen. | In coal-gas. |
|---|---|---|---|---|
| Air . .. .. .. | o | + | + weak | + |
| Nitrogen .. .. | – | – | – strong | – |
| Oxygen . .. .. | + | + | + strong | + strong |
| Carbonic acid .. | – | o | – | – weak |
| Carbonic oxide .. | – | – | – | – weak |
| Nitric oxide . .. | – weak | + | + | .. |
| Ethylene .. .. | – | – | – | – weak |
| Ammonia .. .. | – | – | – | .. |
| Hydrochloric acid | – | – | – weak | .. |

Becquerel was before Faraday in experimenting upon this subject. Becquerel allowed charcoal to absorb gases, and then examined the properties of such charcoal in the magnetic field. He thus discovered the magnetic properties of oxygen to be strong, even in relation to a solution of ferrous chloride, as set forth in the following table:—

*Specific Magnetism, Equal Weights (Becquerel).*

| | | |
|---|---|---|
| Iron .. .. .. .. .. .. .. .. .. | + | 1,000,000 |
| Oxygen .. .. .. .. .. .. .. .. | + | 377 |
| Ferrous chloride solution, sp. gr. 1·4334 | + | 140 |
| Air .. .. .. .. .. .. .. .. .. | + | 88 |
| Water . .. .. .. .. .. .. .. .. | – | 3 |

The lecturer took a cup made of rock salt, and put in it some liquid oxygen. The liquid did not wet rock salt, but remained in a spheroidal state. The cup and its contents were placed between and a little below the poles of an electro-magnet. Whenever the circuit was completed, the liquid oxygen rose from the cup and connected the two poles. Then it boiled away, sometimes more on one pole than the other, and when the circuit was broken it fell off the pole in drops back into the cup. He also showed that the magnet would draw up liquid oxygen out of a tube. A test tube containing liquid oxygen when placed in the Hughes balance produced no disturbing effect. The magnetic moment of liquid oxygen is about 1000 when the magnetic moment of iron is taken as 1,000,000. On cooling, some bodies increased in magnetic power. Cotton-wool, moistened with liquid oxygen, was strongly attracted by the magnet, and the liquid oxygen was actually sucked out of it on to the poles. A crystal of ferrous sulphate, similarly cooled, stuck to one of the poles.

The lecturer remarked that fluorine is so much like oxygen in its properties, that he ventured to predict that it will turn out to be a magnetic gas.

Nitrogen liquefies at a lower temperature than oxygen, and one would expect the oxygen to come down before the nitrogen when air is liquefied, as stated in some text-books, but unfortunately it is not true. They liquefy together. In evaporating, however, the nitrogen boils off before the oxygen. He poured two or three ounces of liquid air into a large test-tube, and a smouldering splinter of wood dipped into the mouth of the tube was not re-ignited; the bulk of the nitrogen was nearly five minutes in boiling off, after which a smouldering splinter dipped into the mouth of the test-tube burst into flame.

Between the poles of the magnet all the liquefied air went to the poles; there was no separation of the oxygen and nitrogen. Liquid air has the same high insulating power as liquid oxygen. The phenomena presented by liquefied gases present an unlimited field for investigation. At –200° C. the molecules of oxygen had only one-half of their ordinary velocity, and had lost three-fourths of their energy. At such low temperatures they semed to be drawing near what might be called "the death of matter," so far as chemical action was concerned; liquid oxygen, for instance, had no action upon a piece of phosphorus and potassium or sodium dropped into it; and once he thought and publicly stated, that at such temperatures all chemical action ceased. That statement required some qualification, because a photographic plate placed in liquid oxygen could be acted upon by radiant energy, and at a temperature of –200° C. was still sensitive to light.

Prof. M'Kendrick had tried the effect of these low temperatures upon the spores of microbic organisms, by submitting in sealed glass tubes blood, milk, flesh, and such-like substances, for one hour to a temperature of –182° C., and subsequently keeping them at blood heat for some days. The tubes on being opened were all putrid. Seeds also withstood the action of a similar amount of cold. He thought, therefore, that this experiment had proved the possibility of Lord Kelvin's suggestion, that life might have been brought to the newly-cooled earth upon a seed-bearing meteorite.

In concluding, the lecturer heartily thanked his two assistants, Mr. R. N. Lennox and Mr. J. W. Heath, for the arduous work they had had in preparing such elaborate demonstrations.

## ON THE
## DENSITIES OF THE PRINCIPAL GASES.*

By Lord RAYLEIGH, Sec. R.S.

(Concluded from p. 200).

### *Reduction to Standard Pressure.*

The pressure to which the numbers so far given relate is that due to 762·511 m.m. of mercury at a temperature of 14·85°,† and under the gravity operative in my laboratory in latitude 51° 47'. In order to compare the results with those of other experimenters, it will be convenient to reduce them not only to 760 m.m. of mercury pressure at 0°, but also to the value of gravity at Paris. The corrective factor for length is 760/762·511. In order to correct for temperature we will employ the formula (Everett, p. 142) $1+0·0001818\,t+0·0000000017\,t^2$ for the volume of mercury at $t°$. The factor of correction for temperature is thus 1·002700. For gravity we may employ the formula—

$$g = 980·6056 - 2·5028 \cos 2\lambda,$$

$\lambda$ being the latitude. Thus, for my laboratory—

$$g = 981·193,$$

and for Paris—

$$g = 980·939,$$

the difference of elevation being negligible. The factor of correction is thus 0·99974.

The product of the three factors, corrective for length, for temperature, and for gravity, is accordingly 0·99914. Thus multiplied, the numbers are as follows:—

| Air. | Oxygen. | Nitrogen. |
|---|---|---|
| 2·37512 | 2·62534 | 2·30883 |

and these may now be compared with the water contents of the globe, viz., 1836·52.

The densities of the various gases under standard conditions, referred to that of distilled water at 4°, are thus:—

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* A Paper read before the Royal Society.

† The thermometer employed with the manometer read 0·15° too high.

| Air. | Oxygen. | Nitrogen. |
|---|---|---|
| 0·00129327 | 0·00142952 | 0·00125718 |

With regard to hydrogen, we may calculate its density by means of the ratio of densities of oxygen and hydrogen formerly given by me, viz., 15·882. Hence—

Hydrogen .. .. .. 0·000090009.

The following Table shows the results arrived at by various experimenters. Von Jolly did not examine hydrogen. The numbers are multiplied by 1000 so as to exhibit the weights in grms. per litre:—

| | Air. | Oxygen. | Nitrogen. | Hydrogen. |
|---|---|---|---|---|
| Regnault, 1847 .. | 1·29319 | 1·42980 | 1·25617 | 0·08958 |
| Corrected by Crafts | 1·29349 | 1·43011 | 1·25647 | 0·08988 |
| Von Jolly, 1880 .. | 1·29351 | 1·42939 | 1·25787 | — |
| Ditto corrected .. | 1·29383 | 1·42971 | 1·25819 | — |
| Leduc, 1891* . .. | 1·29330 | 1·42910 | 1·25709 | 0·08985 |
| Rayleigh, 1893 .. | 1·29327 | 1·42952 | 1·25718 | 0·09001 |

The correction of Regnault by Crafts (*Comptes Rendus*, cvi., p. 1664) represents allowance for the contraction of Regnault's globe when exhausted, but the data were not obtained from the identical globe used by Regnault. In the fourth row I have introduced a similar correction to the results of von Jolly. This is merely an estimate founded upon the probability that the proportional contraction would be about the same as in my own case and in that of M. Leduc.

In taking a mean we may omit the uncorrected numbers, and also that obtained by Regnault for nitrogen, as there is reason to suppose that his gas was contaminated with hydrogen. Thus—

| | Air. | Oxygen. | Nitrogen. | Hydrogen. |
|---|---|---|---|---|
| Mean numbers .. | 1·29347 | 1·42961 | 1·25749 | 0·08991 |

The evaluation of the densities as compared with water is exposed to many sources of error which do not affect the comparison of one gas with another. It may therefore be instructive to exhibit the results of various workers referred to air as unity.

| | Oxygen. | Nitrogen. | Hydrogen. |
|---|---|---|---|
| Regnault (corrected) .. .. | 1·10562 | 0·97138 | 0·06949 |
| Von Jolly (corrected).. .. | 1·10502 | 0·97245 | — |
| Leduc .. .. .. .. .. .. | 1·1050 | 0·9720 | 0·06947 |
| Rayleigh .. .. .. .. .. | 1·10535 | 0·97209 | 0·06960 |
| Mean .. .. .. .. .. | 1·10525 | 0·97218 | 0·06952 |

As usually happens in such cases, the concordance of the numbers obtained by various experimenters is not so good as might be expected from the work of each taken separately. The most serious discrepancy is in the difficult case of hydrogen. M. Leduc suggests (*Comptes Rendus*, July, 1892) that my number is too high on account of penetration of air through the blow-off tube (used to establish equilibrium of pressure with the atmosphere), which he reckons at 1 m. long and 1 c.m. in diameter. In reality the length was about double, and the diameter one-half of these estimates; and the explanation is difficult to maintain, in view of the fact, recorded in my paper, that a prolongation of the time of contact from $4^m$ to $30^m$ had no appreciable ill effect. It must be admitted, however, that there is a certain presumption in favour of a lower number, unless it can be explained as due to an insufficient estimate for the correction for contraction. On account of the doubt as to the appropriate value of this correction, no great weight can be assigned to Regnault's number for hydrogen. If the atomic weight of oxygen be indeed 15·88, and the ratio of densities of oxygen and hydrogen be 15·90, as M. Leduc makes them, we should have to accept a much higher number for the ratio of volumes than that (2·0002) resulting from the very elaborate measurements of Morley. But while I write the information reaches me that Mr. A. Scott's recent work upon the volume ratio leads him to just such a higher ratio, viz., 2·00245, a number *a priori* more probable than 2·0002. Under the circumstances both the volume ratio and the density of hydrogen must be regarded as still uncertain to the 1-1000th part.

## Note A.

### *On the Establishment of Equilibrium of Pressure in Two Vessels Connected by a Constricted Channel.*

It may be worth while to give explicitly the theory of this process, supposing that the difference of pressures is small throughout, and that the capacity of the channel may be neglected. If $v_1 p_1$ denote the volume and pressure of the gas in the first vessel at time $t$, $v_2 p_2$ the corresponding quantities for the second vessel, we have—

$$v_1\, dp_1/dt + c(p_1 - p_2) = 0,$$
$$v_2\, dp_2/dt + c(p_2 - p_1) = 0,$$

where $c$ is a constant which we may regard as the *conductivity* of the channel. In these equations inertia is neglected, only resistances of a viscous nature being regarded, as amply suffices for the practical problem. From the above we may at once deduce—

$$\frac{d\,(p_1 - p_2)}{dt} + \left(\frac{c}{v_1} + \frac{c}{v_2}\right)(p_1 - p_2) = 0\,;$$

showing that $(p_1 - p_2)$ varies as $e^{-qt}$, where—

$$q = \frac{c}{v_1} + \frac{e}{v_2} = \frac{1}{\tau},$$

if $\tau$ be the time in which the difference of pressures is reduced in the ratio of $e : 1$.

Let us now apply this result ($a$) to the case where the globe of volume $v_1$ communicates with the atmosphere, ($b$) to the case where the globe is connected with a manometer of relatively small volume $v_2$. For ($a$) we have—

$$1/\tau = c/v_1,$$

and for ($b$)—

$$1/\tau = c/v_2\,;$$

so that—

$$\tau/\tau' = v_1/v_2.$$

For such a manometer as is described in the text, the ratio $v_1/v_2$ is at least as high as 30; and in this proportion is diminished the time required for the establishment of equilibrium up to any standard of perfection that may be fixed upon.

## THE USE OF ALUM IN BAKING POWDER.

The case of James James, Appellant, *v.* Evan Jones, Respondent, recently decided at Swansea after five days hearing, presents some points of general interest, as it deals with a subject which had previously been little investigated.

It was an appeal to Quarter Sessions from the Justices' decision inflicting a fine for the sale of baking powder of which alum formed a constituent. Omitting the points which are of legal rather than of scientific interest the case may be stated as follows:—

The powder consisted of about 40 per cent potash alum, 22 per cent bicarbonate of soda, and 38 per cent ground rice.

For the respondent, independent experiments by Prof. Dunstan, Prof. Claude Thompson, and Dr. Otto Hehner showed that hydrate of alumina dried at 212° F. dissolved in hydrochloric acid of 0·2 per cent strength, that strength being taken on the authority of the principal physiological treatises as fairly representing the average strength of the free hydrochloric acid in gastric juice.

Prof. Thompson showed that the result was the same when the temperature of drying was raised to 250° F., and the strength of the acid diminished to 0·04 per cent. It was shown that the temperature of the inside of a loaf during baking did not exceed 212° F.

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* *Bulletin des Séances de la Société de Physique.*

Prof. Dunstan, who had fully investigated the matter for the Glamorgan County Council, showed further that the hydrate dried at 212° F. was soluble in the gastric juice of a dog diluted to 0·2 per cent strength, and that the gastric juice of a dog diluted to this extent dissolved hydrate of alumina from bread baked with the powder. That the hydrate of alumina in the bread interfered with the digestion of starch by ptyalin (diastase was used in the actual experiment) and with both peptic and pancreatic digestion. Further, that dilute solution of carbonate of soda of 0·3 per cent strength, the strength of the alkali in intestinal juice, would dissolve hydrate and phosphate of alumina, either freshly precipitated or dried at 212° F., so that absorption of aluminium compounds could occur from the intestine. This was confirmed by his observation that aluminium compounds occurred in the urine of a man who had daily taken 15 to 30 grains of the hydrate dried at 212° F. On one occasion the taking of this quantity of hydrate produced vomiting.

For the appellant, it was contended that the man took much larger quantities of hydrate than would be taken in food, and an attempt was made to draw a distinction between the hydrate as it exists in bread and the hydrate prepared pure and dried at 212° F. No experimental evidence was brought in support of this latter contention.

The experiments with the gastric juice of a dog were objected to on the ground that the gastric juice of carnivora contained a larger proportion of acid than that of man; but, in reply, it was pointed out that the gastric juice of the dog used was diluted to 0·2 per cent—the average strength of human juice.

Mr. W. Morgan, Public Analyst, Swansea, made the following experiment:—He and his son took hydrate of alumina, which had been heated to the temperature of a loaf during baking, either during or after a meal. After about two hours, vomiting was produced by mustard and warm water. The vomit was filtered and the filtrate placed in a dialyser with parchment paper membrane. After leaving all night, aluminium chloride was found to have dialysed. In another experiment, vomiting was produced without taking the hydrate. The vomit was divided into two portions; one was dialysed directly, the other after warming with the hydrate at 105° F. On examination, aluminium chloride was found in the dialysed liquid in the latter case, while none could be found in the blank experiment.

It was contended that these experiments were unfair because the hydrate was used as such, and not in bread. The experiment was repeated for the appellant by Dr. Luff, the Official Analyst to the Home Office, Mr. Sutton, and Dr. Blyth, on one of the witnesses for the appellant during the hearing of the case, with the modification that the man was fed with 1 lb. of bread made with the baking powder, and that the bladder of a recently killed sheep was used as a membrane. It was objected by the respondent that this experiment might be inconclusive, for in view of the use made of aluminium salts in tanning, it could not be expected that aluminium chloride would dialyse through fresh bladder. The bladder was also only washed with cold water, and was therefore presumably not free from mucus. In reply to this the bladder was subsequently tested and found free from aluminium compounds. It was further objected that the man drank 1½ pint of water while eating the bread. This would greatly dilute the gastric juice. The total amount vomited was about 1 pint, so that the quantity of aluminium compound present could not have been large. The dialysed liquid was only tested by adding ammonia after boiling with nitric acid; it was not evaporated and ignited to destroy organic matter.

Dr. Lauder Brunton gave evidence as to the astringent action of aluminium chloride, and generally as to the injurious effects likely to ensue from the absorption of aluminium compounds.

It was contended on behalf of the respondent that these experiments proved that hydrate of alumina was soluble in the digestive canal, and would produce the same injurious effects as alum; that it would have an irritant and astringent action on the membrane of the stomach, and would interfere with digestion. Further, that absorption of some aluminium compound was proved, and that the introduction into the system of an entirely foreign element could hardly fail to be injurious.

On behalf of the appellant practically no attempt was made to prove that alum itself was not injurious. It was, however, admitted by the respondent that, by the action of the bicarbonate of soda in the powder, it was completely converted into hydrate of alumina; and it was contended by the appellant that this hydrate was insoluble in the digestive canal, and, as an inert substance, passed unchanged through the body; its small amount (6 grains hydrate per pound of bread) would render it perfectly harmless. Further, that if it did dissolve, the small quantity of chloride of aluminium formed would be harmless.

Before the hearing of the case the following experiments had been made in support of the contention that the hydrate was an inert body:—

Mr. Sutton some years ago fed pigs for eight days exclusively with bread made with the baking-powder. They throve well, and after death alumina was detected in the contents of the intestine, while none could be found in the blood or in the urine contained in the bladder at death. In reply it was contended that the first result proved nothing; with regard to the second the quantity of urine examined was too small for a negative result to prove conclusively that no absorption had taken place. Further, there was no evidence that the pigs were not, as usual, fasted for twenty-four hours before slaughter; if this were done it might materially influence the result.

Dr. Luff prepared hydrate of alumina which was dried at 300° F. Several portions of the "dried hydrate of alumina" were treated with 35 to 40 c.c. each of hydrochloric acid of 0·02 per cent strength, which Dr. Luff stated he believed to be the strength in the gastric juice in the human body.

Eight tubes were warmed to 98·4° F., and one was tested at the end of each hour in the following manner:—On filtering and adding ammonia no precipitate was obtained, even if the filtrate was previously concentrated.

In criticism of these experiments it was contended, first, that the temperature at which the substance was dried greatly exceeded that in the interior of a loaf during baking. The substance was not analysed; there was no proof that it was hydrate of alumina at all, as it might have lost water. Proof of its composition was all the more necessary as a sample of "dried hydrate of alumina" had on a previous day been handed up to the Bench by Mr. Sutton, which had been heated to low redness and was afterwards admitted to be oxide. Secondly, that the strength of the hydrochloric acid used did not fairly represent the strength of the acid in gastric juice, which was generally accepted as about 0·2 per cent instead of 0·02 per cent. When asked for his authority Dr. Luff referred to a Table given in "Halliburton's Chemical Physiology," and stated that recent experiments showed that the strength 0·2 per cent was too high. It was, however, shown by the respondent that the Table in "Halliburton" was taken from the experiments of Schmidt, published in 1855, and that Halliburton, while quoting the results, actually pointed out that the acidity was below the normal, possibly owing to the juice having been obtained from a woman with gastric fistula. Halliburton, like other physiologists, accepted 0·2 per cent as the strength to be used in making artificial gastric juice.

Dr Luff admitted in cross examination that he had made no notes of these experiments, and stated that it was not his habit to make notes of merely qualitative experiments.

Dr. Richardson stated his opinion that the powder was harmless. He said that he did not consider it proved that aluminium chloride was formed in the stomach, and that even if aluminium chloride were formed, it could not be absorbed as it coagulates the blood. It was pointed out that it was not contended that aluminium was absorbed as chloride and that chloride of iron was given as a medicine in cases of anæmia. Dr. Richardson said that it was not proved that iron was absorbed in such cases. He declined to make any statement as to the strength of the acid in the gastric juice.

Dr. Winter Blyth expressed his opinion that the baking-powder was not injurious. He brought forward no experiments, except the one already described, performed whilst the case was in progress. He stated that if injury were caused by alum baking-powders it must have become known to medical officers of health.

Many medical men were called and expressed the opinion that the baking-powder was not injurious, stating that they had either used it themselves in their families or had known it used by others without harmful results. Other witnesses also stated that they had used it without harm. It was, however, shown that in most cases the quantity used was very small, much smaller than would be taken by a person feeding largely on bread baked with the powder.

The appeal was dismissed with costs, and the conviction affirmed.

## PROCEEDINGS OF SOCIETIES.

### ROYAL INSTITUTION OF GREAT BRITAIN.

*Annual Meeting, Monday, May 1, 1893.*

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1892, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £104,000, entirely derived from the contributions and donations of the members and of others appreciating the value of the work of the Institution.

Sixty-three new members were elected in 1892.

Sixty-three lectures and twenty evening discourses were delivered in 1892.

The books and pamphlets presented in 1892 amounted to about 238 volumes, making, with 530 volumes (including periodicals bound) purchased by the managers, a total of 768 volumes added to the library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as officers for the ensuing year:—

*President*—The Duke of Northumberland, K.G., D.C.L., LL.D.

*Treasurer*—Sir James Crichton-Browne, M.D., LL.D., F.R.S.

*Secretary*—Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M.Inst.C.E.

*Managers*—Captain W. de W. Abney, C.B., R.E., D.C.L., F.R.S.; Shelford Bidwell, M.A., F.R.S.; John Birkett, F.R.C.S.; Joseph Brown, C.B., Q.C.; Sir Douglas Galton, K.C.B., D.C.L., LL.D., F.R.S.; David Ed. Hughes, F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; George Matthey, F.R.S.; Hugo Müller, Ph.D., F.R.S.; The Right Hon. Earl Percy, F.S.A.; William Chandler Roberts-Austen, C.B., F.R.S.; Sir David Salomons, Bart., M.A., F.R.A.S., F.C.S.; Alexander Siemens, M.Inst.C.E., Basil Woodd Smith, F.R.A.S., F.S.A.; Sir Richard Webster, M.P., Q.C., LL.D.

*Visitors*—Charles Edward Beevor, M.D., F.R.C.P.; Henry Arthur Blyth; Francis Woodhouse Braine, F.R.C.S.; John Tomlinson Brunner, M.P.; Michael Carteighe, F.C.S.; Rookes Evelyn Crompton, M.Inst.C.E.; James Farmer, J.P.; Robert Hannah; Donald William Charles Hood, M.D., F.R.C.P.; Raphael Meldola, F.R.S.; Lachlan Mackintosh Rate, M.A.; Boverton Redwood, F.C.S.; John Callander Ross; John Bell Sedgwick, J.P., F.R.G.S.; George Andrew Spottiswoode.

## NOTICES OF BOOKS.

*A Dictionary of Applied Chemistry.* By T. E. Thorpe, B.Sc. (Vict.), Ph.D., D.Sc. (Dublin), F.R.S. Assisted by Eminent Contributors. In Three Volumes. Vol. III. London and New York: Longmans, Green, and Co. 1893. 8vo., 1058 pp.

This concluding part of Dr. Thorpe's great work is fully on a level with the two preceding volumes.

Concerning noble opal, we learn that the Hungarian mines of this precious stone still employ two hundred workmen.

The recent extension of the cultivation of opium is a remarkable fact. As far back as 1882 the annual production in the South-West of China was more than twice the whole importation from India. In a few years the use of Indian opium, if it survives at all, will be confined to a few wealthy connoisseurs. Hence it follows that the anti-opium agitation will soon lose its *raison d'être.* It follows also that the alleged anxiety of the Chinese Government to suppress opium-smoking is not *bonâ fide.*

The section on pigments is exceedingly elaborate, though we find no mention of mineral lake, stannic chromate, a colour closely resembling in tone the lighter madder-lake, but according to Gentele absolutely permanent.

Pure scarlet mercuric iodide, known also as geranium red, is certainly inferior to vermilion in permanence. We have observed, however, that, obtained in the dry way by grinding up mercury with a sufficient proportion of iodine,—the reaction being attended with the development of light and heat,—it is much less fugitive than if prepared in the moist way.

The writer distinguishes carmine from cochineal lakes, as containing a larger proportion of colouring matter and less alumina.

To the dyer and tissue-printer it sounds strange to hear indigo characterised as "very fugitive."

As regards the metallurgy of platinum, the eminent merit of Messrs. Johnson, Matthey, and Co. is fully and justly shown.

The articles on sodium, spectrum analysis, and sulphur may almost be regarded as monographs of their respective subjects.

Under tea we find mention of some very interesting facts. The consumption of tea in Australia amounts to 9 lbs. per head; in China, in Britain, and South Africa, 5 lbs.; in Holland, 0·91 lb.; and in Russia, 0·43 lb. In France, Germany, &c., the consumption of tea is insignificant. It is a remarkable fact mentioned here, though not explained, that Chinese tea keeps better than the produce of India and Ceylon. A fact which should interest the consumer is that in five minutes boiling water extracts practically all the theine, the essential oil, but not more than one-third of the tannin. Robert Fortune is here quoted as including Ireland among the parts of the earth best suited for the cultivation of the tea-plant, whilst in the next sentence we read that a "warm climate is essential, and that in the best districts of China the ordinary range of the thermometer in the summer at 3 p.m. is between 80° and 90°."

A great advantage of Indian tea is its superior cleanliness, as machinery is almost exclusively used in its manufacture. The significance of this point will be appreciated if we remember the intense dirtiness of the Chinese working population.

Under tellurium we are reminded that, according to Brauner, it is probably a mixture of true tellurium with some unknown bodies.

Under tobacco we find it stated—as we believe with full truth—that its growth in Britain, as a field crop, did not in 1886 receive a fair and full trial. The use of kainite and common salt as manures was a complete mistake. Where potash was deficient it should have been supplied in the state of sulphate. It is to be noted that whilst in England the home cultivation of tobacco was suddenly and harshly stopped in 1782, the plantations being destroyed and the planters heavily fined and imprisoned, in Ireland it survived down to 1831.

The article on water is ably and comprehensively written. The notion of "previous sewage contamination" is not accepted. The celebrated "Recommendations" of the Royal Rivers Commission are not quoted, and no unitary method is laid down for dealing with polluted waters. The question as to the relative sanitary value of hard and soft waters is very fairly handled, the conclusion being that the difference of their action upon human health is not well marked. For technical purposes the necessity of pure water is, however, strongly insisted upon.

Under wine we read that vines are very apt to degenerate in a novel district. French vines have not given satisfaction in America, and, on the other hand, American vines transplanted to the Gironde "yielded no potable wine." These latter experiments are much to be deplored, since they seem to have introduced the phylloxera into Europe. But, on the other hand, European vines do not appear to have degenerated in Australia.

The author's opinion concerning "plastered" wines is decidedly condemnatory. But the attempts at "deplastering" have been decidedly mistaken. They have depended on the use of barium and strontium salts. The salts of barium, if in the slightest excess, are distinctly poisonous. Strontium is not in itself a poison, but its compounds rarely occur in nature absolutely free from barium salts.

The limit fixed in certain counties for the toleration of gypsum in wine (=2 grms. potassium sulphate per litre) seems too lax. The true standard would be the condemnation and destruction of all wines containing more sulphuric acid (free and combined) than is naturally present in grape juice. It is said that an addition to wines of calcium phosphate produces all the good results alleged to be obtained by "plastering" without its disadvantage.

Dr. Thorpe's great work carries with it its own emphatic recommendation. It must prove most valuable, not merely to chemists and chemical manufacturers, but to all merchants who have to deal with chemical products.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 16, April 17, 1893.

**Detection of the Higher Alcohols and other Impurities in Vinic Alcohol.**—Emile Gossart.—The method of analysis depends on the observation of the rollings of drops of known composition falling from the height of 1 m.m. with an interval of 30″ on a meniscus of a plane slope.

**The Hygroscopic Properties of Various Textile Substances.**—Th. Schlœsing (Fils).—This paper cannot be reproduced without the accompanying diagram.

**Contribution to the Study of the Leclanché Battery.**—A. Ditte.—The author examines the behaviour of an element consisting of a rod of zinc attached to a plate of platinum and immersed in a 10 per cent solution of sodium chloride. The upper part of the zinc becomes covered with a layer of oxide, which descends along the rod and then spreads out horizontally, separating the liquid into two strata, the upper portion being alkaline and free from zinc, whilst the lower remains neutral and contains zinc chloride.

**Attempt at a General Method of Chemical Synthesis. Formation of Nitro-Compounds.**—Raoul Pictet.—It appears from the author's experiments that all the nitrifications of naphthaline, phenol, and toluol are profoundly modified by the methodical use of low temperatures along with the utilisation of electric energies introduced from without.

**Stereochemistry of Malic Compounds and the Variation of the Rotatory Power of Liquids.**—Albert Colson.—The author asserts that the derivatives of malic acid readily yield substances which are exceptions to the rule of the product of asymmetry. Such a substance is acetylmalic acid, $C_6O_6H_8$.

**Iron Chlorobromide.**—C. Lenormand.—The compound in question, $Fe_2Cl_2Br$, is obtained by causing bromine to act very gradually upon anhydrous ferrous chloride. It forms dark crystals, green by reflected light, and very deliquescent.

**Calcium Sucrates.**—P. Petit.—A thermochemical paper not suited for useful abstraction.

**New Soluble Ferment which Splits up Trehalose into Glucose.**—Em. Bourquelot.—The author has found this ferment in a mould of *Aspergillus niger*, which may be preferably cultivated on Raulin's liquid. It is accompanied by another ferment which acts upon maltose, and which the author names *maltase*, the former ferment being *trehalase*.

**Influence of the Pressure of Gases upon the Development of Plants.**—Paul Jaccard.—As a general rule, the changes of pressure in the atmosphere surrounding a plant exert a considerable influence upon its development. The intensity and the nature of the phenomenon vary naturally more or less according to the species, but the general curve representing the variations of development with pressure has ordinarily two maximum points: the first, by far the most marked in the depressed air, and the second, in the compressed air; the normal pressure is, then, most frequently between the two maxima. Although the tension of the oxygen plays a preponderating part in the phenomenon, the action of the absolute pressure is also manifest. It may be said that the action exerted by atmospheric pressure within limits compatible with the existence of organisms is not the same in chlorophyllic plants as in animals.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 7.

**Copper Oxybromide Analogous to Atacamite.**—J. Dupont and H. Jansen.—The authors obtain this compound by heating cupric oxide to 200° in a sealed tube along with cupric bromide.

**Certain Points of Stereochemistry.**—Albert Colson.—A continuation of the polemic against M. Friedel and Le Bel.

**On Inuline: Pseudo-Inuline and Inulénine.**—M. Tanret.—Pseudo-inuline after desiccation at 130° gave—

$$\left.\begin{array}{l}C = 43{\cdot}94\\ H = \ \ 6{\cdot}32\end{array}\right\} C_{192},H_{162},O_{162}.$$

It does not reduce Fehling's liquid. The composition of inulénine is—

$$\left.\begin{array}{l}C = 43{\cdot}47\\ H = \ \ 6{\cdot}48\end{array}\right\} C_{120},H_{104},O_{104}.$$

### *Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxi., No. 3.

**Determination of Slag in Puddled Irons.**—L. L. de Koninck.—The author combats the objection raised by Barrow and Turner (*Journ. Chem. Soc.*) against the use of gaseous chlorine.

### *Bulletin de la Société d'Encouragement pour l'Industrie Nationale.*
Series 4, Vol. viii., No. 87.

**On the Metallic Carbonyls.**—Ludwig Mond.—Translated from the *Journ. Soc. Chem. Ind.*

### *Zeitschrift fur Analytische Chemie.*
Vol. xxxi., Part 6.

(For some unexplained reason the issue of this concluding part of Vol. xxxi. has been delayed until after the appearance of Vol. xxxii. has commenced.)

**Wine Statistics of Germany.**—A continuation of an elaborate report on the wines produced in Germany, of little interest in other countries.

**Method for the Quantitative Determination of Arsenic.**—Helge Bäckström.—This paper will be inserted in full.

**Apparatus for Reducing the Readings of the Barometer to 760 m.m.**—A. W. J. Bockhout.

**Arrangement for Closing Sulphuretted Hydrogen Apparatus.**—Heinrich Trey.

**Continuous Action Suction and Pressure Apparatus.**—W. Reatz.—These three papers cannot be intelligibly reproduced without the eight accompanying figures.

**Oxidising and Decolourising Action of Charcoal.**—P. Cazeneuve.—Already inserted.

**Composition of Glass Suitable for Chemical Vessels.**—R. Weber (*Berg. und Hütten Zeitung*) gives the following composition:—

| | |
|---|---|
| Silica | 74·10 |
| Alumina | 1·90 |
| Lime | 9·75 |
| Potassa | 6·70 |
| Soda | 10·55 |
| | 100·00 |

The glass remained perfectly bright on exposure to air and in contact with hydrochloric vapours. A flask holding 100 c.c. on boiling in water for six hours lost 8 m.grms.

**A Dialyser.**—Gautier.—(From the *Bull. Soc. Chim. de Paris.*

**Recognition of the Temperature at which Petroleum begins to Evolve Gases and Vapours which may Explode on Admixture with Air.**—A. Gawalowski (*Oel und Felt Industrie*).—On a sand-bath heated from below by a small flame is placed a capsule containing the substance in question. Over it is turned a cylinder of glass 8 to 10 c.m. in length, contracted at its upper end, and provided below with three notches. Through each of two of these notches passes a glass tube bent upwards below the cylinder, one of which is drawn out to a point and connected with the gas-pipe. In experiments a very small flame is allowed to burn at the point of the tube, whilst the other glass tube above mentioned introduces a direct supply of atmospheric air. As soon as the temperature is reached at which combustible gases are evolved there ensue small detonations. The temperature is read off on a thermometer which dips into the liquid. For determining the flashing-point the author fixes on the cylinder, which in this case is open above a small top-piece, and over it a cap of wire netting. The tube conveying air is removed, and above the wire netting there is held a small gas flame until the gases ignite. If no gas is at hand a small wax taper may be used. In another arrangement, devised by the same author, which acts more accurately and also automatically, the oil is heated in a closed kettle, on the cover of which is fixed a Finkener burner. The petroleum vapours ascend in the mixing-tube of this burner and mix with the air admitted through a lateral opening. Near the upper aperture is a small flame which effects the ignition of the gaseous mixture as soon as a sufficiency of petroleum vapour is present. To the upper aperture of the burner-tube there is soldered a small hook, by means of which a valve is kept freely suspended by means of a cotton thread saturated with ammonium nitrate. At the moment when the mixture of gas and air is ignited the thread burns, the valve closes automatically and prevents the further escape of petroleum vapours from the small kettle.

**Balances of Precision.**—Two balances for rapid weighing have been proposed respectively by A. Collot, Fils (*Bull. Soc. Chim. de Paris*, iii., 61 and 98) and Victor Serrin (*Comptes Rendus*, cxii, 1299).

**Photometric Apparatus**, all for photographic purposes, have been devised by F. Hurter, E. G. Ballard, Driffield, and have been discussed by W. M. W. Abney. Particulars are not here given, but may be found in the *Journ. Soc. Chem. Industry.*

**Laboratory Appliances used at the Connecticut Agricultural Station.**—S. W. Johnson.—(From the *Journal of Applied Chemistry*).

**Rapid Determination of Carbon Dioxide in Chimney Gases.**—H. Sæger and Jul. Aaron (*Thon. Industrie Zeitung*).—The authors' method does not admit of explanation without the accompanying figure.

**Measuring Instrument for Liquids.**—Alex. F Reid.—(From the Chemical News).

**Backstroke Valve for Water Air-Pumps.**—C. Haase (*Chemiker Zeitung*).—This paper requires the accompanying illustration.

**Preservation of Constant Temperatures above the Boiling-Point of Water.**—K. Ulsch (*Zeit. fur Brauwesen*).—Already inserted.

**A Desiccator.**—F. Soxhlet (*Zeit. Angew. Chemie*).—Requires the four accompanying figures.

**Water-Baths of Porcelain.**—B. Fischer and W. Dittmar (*Chemiker Zeitung*).—Such water-baths are preferable to those of copper, both on account of their cleanliness and cheapness.

**A Cooler.**—E. Greiner (*Zeit. Angew. Chemie*).—An internal vessel is inclosed in a double glass jacket, traversed by a current of cold water.

**Lixiviation Apparatus for the Determination of Fats.**—F. Geisler (*Oel. und Felt Industrie*).—This paper requires the accompanying figure.

**Purifying and Drying Coal-Gas.**—A. Gawalowski.—For the description of the apparatus we must refer to the original. As a desiccating material the author uses burnt lime, slacked with a solution of ferric oxide, and then strongly dried.

**A New Form of Flexible Tubes for Gas.**—T. R. Almond (*Engineering and Mining Journal*).—A double system of wine spirals.

**Bottles of Lead for Hydrofluoric Acid.**—J. L. C. Eckelt (*Chemiker Zeitung*).—The bottles contain 100, 250, and 500 grms. of acid. They are mounted in blocks of wood, in which they may be conveyed after the wooden lid is screwed down.

**Examination of Ammonia for Carbonic Acid.**—J. Hertkorn (*Chemiker Zeitung*).—The author proposes the rule that a mixture of ammonia and lime-water should show only a slight turbidity on boiling.

## MISCELLANEOUS.

**An International Food-Law.**—The *Chem. Zeitung* in a leader on the absence, in Austria, of any general legislation on the sale of food, raises the important but difficult question of an international agreement on sophisticated or substituted articles of food and consumption.

**Alleged Occurrence of Helium.**—Prof. Poplin, a Government Analyst in the United States, is said (in the *Chemiker Zeitung*) to have discovered a new element in a meteorite which he is examining. He observed in the spectroscope lines corresponding to those observed by Prof. Angström, and referred by him to "helium"—a hypothetical element not detected in any terrestrial mineral. The *Pall Mall Gazette* of April 24 gives a similar account, and adds that the meteorite came from the direction of the constellation Perseus and fell in Missouri. It was found to contain 25 per cent of an unknown metal. In neither case is the original authority given.

**The Thermo Hydrometer.**—In the determination of specific gravities serious errors will be introduced unless the temperature of the liquid is accurately taken simultaneously with the reading of the hydrometer. We have received from Messrs. Fletcher, Fletcher, and Stevenson, North London Chemical Works, one of their new Thermohydrometers, in which the bulb of the thermometer is blown in one piece with the bulb of the hydrometer and comes into direct contact with the liquid to be tested. The stem of the thermometer is inside the stem of the hydrometer, and the two scales being engraved on the same strip of ivory both can be read simultaneously. The thermometer scale is graduated from −10 to +50° C., and the hydrometer from 1000 to 1050. To all who require frequent observations of specific gravity this instrument will be invaluable.

## MEETINGS FOR THE WEEK.

Monday, 8th.—Society of Arts, 8. "Mosaic—its History and Practice," by C. Harrison Townsend. (Cantor Lectures).
—— Royal Institution, 5. (General Monthly Meeting).
Tuesday, 9th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Royal Institution, 3. "Modern Society in China," by Prof. R. K. Douglas.
—— Society of Arts, 8. "Primitive Art in Egypt," by Prof. W. M. Flinders Petrie.
Wednesday, 10th.—Society of Arts, 8. "The Richmood Lock and Tidal Weir," by J. B. Hilditch.
—— Geological, 8.
Thursday, 11th.—Royal Institution, 3. "The Atmosphere," by Prof. Dewar, F.R.S.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
Friday, 12th.—Royal Institution, 9. "Isoperimetrical Problems," by Lord Kelvin, Pres.R.S.
—— Astronomical, 8.
—— Physical, 5. "The Drawing of Curves from their Curvature," by C. V. Boys, F.R.S. "The Foundations of Dynamics," by Oliver Lodge, F.R.S.
Saturday, 13th.—Royal Institution, 3. "Johnson and Milton," by Henry Craik, LL.D.

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We, the undersigned, Joshua Beck and Wallace Shawcross, Trustees of the Will of the late James Farmer, HEREBY GIVE NOTICE that we have sold the business of Chemical Manufacturers, carried on by us as such Trustees at Gorton Brook Chemical Works, Manchester, under the style of James Farmer, to John Gibson and Co., of Medlock Chemical Works, Manchester, who will, from and after the 17th instant, carry on such business for their own benefit under the style and title of "James Farmer." AND WE HEREBY GIVE FURTHER NOTICE that neither we nor the estate of the late James Farmer will be responsible for any debts contracted in respect of such business on or after the 17th instant.

Dated this 17th day of April, 1893.

Signed in the presence of
RICHARD HILDITCH,
Solicitor,
Manchester.

JOSHUA BECK,
WALLACE SHAWCROSS.

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## PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that The Chemische Fabrik auf Actien (Vorm E. Schering), of 170, Müller Strasse, Berlin, Germany, has applied for leave to amend the Specification of the Letters Patent No. 15,404 of 1890, for "Improvements in the Manufacture of Spermine," granted to Wilhelm Majert.

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 26th April, 1893.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of the opposition to the Amendment within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
Comptroller General.

## PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that The Chemische Fabrik auf Actien (Vorm E. Schering), of 170, Müller Strasse, Berlin, Germany, has applied for leave to amend the Specification of the Letters Patents No. 11,957 of 1891, for "Improvements in the Manufacture of Piperazine or Spermine." granted to Wilhelm Majert.

Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 26th April, 1893.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of the opposition to the Amendment within one calender month from the date of the said Journal.

(Signed) H. READER LACK,
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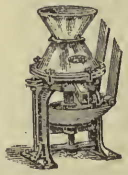

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1746.

# ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.[*]

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 209).

### *Croft's Red Potassium Chrom-Oxalate* (5), $K_2Cr_2 4C_2O_4+8H_2O$ or $12H_2O$.

I now made some of this salt according to Croft's directions. By the action of fifty-five parts by weight of crystallised oxalic acid on a solution containing nineteen parts of potassium dichromate, then evaporated to small bulk and put aside to crystallise, after the lapse of several weeks the salt was obtained. The crystals were dissolved in water, and gave the following absorption-spectrum (5).

Continuous absorption ending about 800, then a faint shadowy band at 710; then two thin dark bands having their centres at 704 and 695 respectively; then two faint incidental bands at 681 and 663 respectively. The broad absorption from 633—502, and continuous absorption from about 467.

It would thus appear that this spectrum with the dark double lines at 704 and 695 is typical of the salts of the formula $M_2'Cr_2 4C_2O_4$. Now, it has been shown that this is the absorption-spectrum given by the first action of oxalic acid on a solution of chromium oxalate, and which for the reasons mentioned previously is undoubtedly the absorption-spectrum of the hydrogen compound of the series $M_2'Cr_2 4C_2O_4$.

Further, it has been shown that with more oxalic acid and when the solution is heated the band 695 disappears, while the remaining incidental bands together with the dark band at 704 become darker, and we have an absorption-spectrum identical with that given by the salts of the general formula $M_6'Cr_2 6C_2O_4$. Now since in neither case is there present any metal corresponding to M', but hydrogen only, it follows that the absorption-spectrum given must be due to the hydrogen compound of this series.

The constitution of these two series of salts—$M_6'Cr_2 6C_2O_4$ and $M'_2Cr_2 4C_2O_4$—is not that of double salt, as in that case their absorption-spectra would not differ from that of chromium oxalate, but is rather that of salts of two acids—$H_6Cr_2 6C_2O_4$ and $H_2Cr_2 4C_2O_4$ respectively. It is for this reason that these compounds have been designated chrom-oxalates throughout this paper.

### *Other Analogous Oxalates.*

It is well known that the double oxalates of the alkalis with iron, manganese, and cobalt possess exceptional colours; thus the ferric salts are usually yellow, while potassium ferric oxalate has a fine green colour resembling the ferrous salts. Again, the cobalt salts are either blue when anhydrous or red when hydrated, while potassium cobaltic oxalate has a beautiful green colour not unlike the colour of nickel salts.

With the above facts in view, and also what has been already stated relative to the constitution of the chrom-oxalates, it was thought desirable to study the spectroscopic relations of these compounds.

The double ammonium and potassium salts of ferric, manganic, cobaltic, and cupric oxalates were prepared and spectroscopically examined.

### *Ammonium Ferric Oxalate*, $(NH_4)_6Fe_2 6C_2O_4+6H_2O$ (No. 6).

This salt was dissolved in water, and a layer of the solution having a thickness of 6·4 c.m. was examined. This gave continuous absorption to 698, shading off to 623, and then continuous absorption from 489 to the end of the spectrum (6).

It is known that this salt, together with others, is decomposed by light, and some experiments were made to determine the limits of the more active rays effecting this decomposition. Glass tubes containing the salt in solution were put into clear colourless glass bottles, the latter containing respectively concentrated solutions of the following bodies:—Ammonium copper sulphate, potassium dichromate, ammonium ferric oxalate (which was frequently changed as it became decomposed), and copper chloride. The bottles and tubes were then securely covered with opaque paper which reached just below the surface of the liquid in the outer vessel, so that the only light which penetrated to the tube containing the solution under experiment passed through a protecting layer of the above solutions, having a thickness of 2 c.m. The absorption-spectrum given by a layer of this thickness of protecting liquid was then determined, with the following result:—

| | Continuous absorption. | Continuous absorption. |
|---|---|---|
| 1. Ammonium copper sulphate .. | 500 | 418 |
| 2. Potassium dichromate .. .. | 717 | 543 |
| 3. Cupric chloride.. .. .. .. | 608 | 480 |
| 4. Ammonium ferric oxalate .. | 698 | 465 |

The ammonium ferric oxalate solution under experiment was completely decomposed after standing in (1) ammonium copper sulphate after two days exposure to sunlight.

In (2) potassium dichromate solution no decomposition occurred even after standing five days.

In (3) cupric chloride very slight decomposition resulted after standing five days.

In (4) ammonium ferric oxalate there was a greater amount of decomposition than in the case of (3) after standing the same time, viz., five days.

From these experiments the more active rays are those lying between 480 and 418.

It is worthy of note that these rays, which were transmitted by the above thickness of ammonium ferric oxalate, were still able to produce a certain amount of decomposition in that salt, although the protecting layer of ammonium ferric oxalate was frequently changed as it was decomposed. These experiments were made in the summer months.

### *Potassium Ferric Oxalate*, $K_6Fe_2 6C_2O_4+6H_2O$.

This salt gave in solution a similar absorption-spectrum, continuous absorption to 698, then a slight shadow to 627, and continuous absorption again from 489.

The crystals of this salt were also examined, but no definite bands could be observed.

In order to see if ferric oxalate behaved differently when dissolved in oxalic acid, the experiment was made, and it was found that there was much less absorption in this case in the less refrangible part of the spectrum, the continuous absorption reaching only to 790, as compared with 698 in the double salt.

### *Potassium Manganic Oxalate*, $K_6Mn_2 6C_2O_4+6H_2O$ (7).

This was the next salt examined. It is easily made by the action of manganese dioxide on a solution of acid potassium oxalate. It is very unstable, and requires to be examined immediately. The solution was of a fine dark red colour, but no absorption bands were observed, only continuous absorption from 704 and 601 respectively.

The corresponding ammonium salt gave the same absorption-spectrum.

### *Potassium Cobaltic Oxalate*, $K_6Co_2 6C_2O_4+6H_2O$ (8).

This salt has been fully described by Kehrmann and Pickersgill (*Ber.*, xxiv., 2324, 1891) as crystallising in nearly black prisms, which are dichroic—blue and green.

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[*] *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

It yields a fine dark green solution, which gives a broad absorption band in the green part of the spectrum. My measurements are as follows:—Continuous absorption to 770, with a shadow to 710; then a broad absorption band from 657 to 543, and continuous absorption from 469.

*Potassium Cupric Oxalate*, $K_2Cu2C_2O_4+2H_2O$ (9).

This salt was next examined; it yields a blue solution like the other cupric salts; a thickness of 9·2 c.m. of solution was used in examining its absorption-spectrum. In this case also no absorption bands were visible, only continuous absorption to 639 and from 411. The crystals of this salt were also examined, but with a similar result as the above. The same remark applies to the ammonium salt, which was also examined.

As the foregoing oxalates have now been shown not to give characteristic absorption-spectra, it is therefore impossible to determine their constitution by the same spectroscopic methods which have been used for the corresponding chrom-oxalates, but I thought that the results obtained were worth recording.

*Analogous Compounds with Malonic Acid.*

Having shown how the various chrom-oxalates are related spectroscopically to each other, to chromium oxalate, and also to the analogous oxalates of other metals, it was thought desirable to search for similar compounds in the case of various organic acids. The first which naturally suggests itself is the homologue of oxalic acid, viz., malonic acid.*

In the following experiments the acid was allowed in some cases to act in the cold on an excess of chromium hydroxide. In other cases the acid was in large excess, and heat was applied, when that was possible without decomposition.

Various specimens of chromium hydroxide were prepared, and precautions were taken to have it free from fixed alkali. Thus pure chromium trioxide dissolved in water was reduced by alcohol and precipitated by ammonia solution in excess. The resulting precipitate of chromium hydroxide was well washed by decantation, and thrown on a filter, and again well washed. This was re-dissolved in hydrochloric acid and re-precipitated, as before, by ammonia solution, and washed till the washings gave no precipitate with a solution of silver nitrate acidified with nitric acid. Duplicate experiments were made; in all cases using a different specimen of chromium hydroxide. In some other cases, another specimen of the acid was procured from an entirely different source, but with a like result in all cases.

*Malonic Acid*, $CH_2(CO_2H)_2$ (11).—A strong aqueous solution of this acid easily dissolves freshly precipitated chromium hydroxide. The solution has a fine bluish purple colour, and gave the following absorption-spectrum:—

Continuous absorption to 714, then a band from 695—689, then a shadow from 655 joining the broad absorption from 623—503, and continuous absorption from 464.

On comparing this spectrum with that given by chromium oxalate, it is similar in character, but does not appear to be identical with it; for, as the result of repeated observation, the centre of the band in the red part of the spectrum is moved slightly nearer the more refrangible end. It is also somewhat darker, while the broad absorption appears about the same in both.

An excess of malonic acid added to this solution does not appear to influence the absorption-spectrum. In this respect also it differs from oxalic acid in its action on chromium oxalate.

A little ammonium malonate was now added to the solution of chromium hydroxide in malonic acid, and the solution warmed. The resulting solution gave an absorption spectrum differing from the above, but similar in character to that given by the chrom-oxalates of the general formula $M'_6Cr_26C_2O_4$, and from this it was believed that a similarly constituted compound was produced. The ammonium malonate was, in another experiment, replaced by potassium malonate, with a like result spectroscopically. It was found that the ammonium salt did not crystallise so well as the potassium salt, therefore some quantity of the latter was prepared, by the action of an excess of freshly precipitated chromium hydroxide on a solution of acid potassium malonate. The action takes place easily if the chromium hydroxide is freshly precipitated. This solution gives an extremely dark band, its centre being 701.

If an excess of the acid has been used, or what is the same thing, if the chromium hydroxide is not in sufficient quantity, or if it has been insufficiently digested, two dark bands in the red part of the spectrum appear, as is the case with the oxalate under similar conditions. Two hours digestion was usually found sufficient. It was then filtered, evaporated to small bulk, and it was then placed over sulphuric acid, when the salt crystallised out. As it is extremely soluble in water, it is somewhat difficult to crystallise. In some cases, when the crystallisation was imperfect, the crystals were washed with alcohol.

The salt was analysed and the following numbers obtained:—

| Grm. | | At 120° C. Grm. | | P.c. | | P.c. |
|---|---|---|---|---|---|---|
| 0·7865 | lost | 0·0812 | = | 10·32 $H_2O$ | | |
| 0·7865 | gave | 0·1200 $Cr_2O_3$ | = | 15·24 $Cr_2O_3$ | = | 10·45 Cr |
| 1·2532 | gave | 0·1839 $Cr_2O_3$ | = | 14·66 $Cr_2O_3$ | = | 10·06 Cr |
| 1·7030 | gave | 0·2540 $Cr_2O_3$ | = | 14·97 $Cr_2O_3$ | = | 10·30 Cr |
| 0·6810 | gave | 0·2787 KCl | = | 40·93 KCl | = | 21·47 K |

| | $K_6Cr_26(C_3H_2O_4)+6H_2O$. Calculated. | Found. | | |
|---|---|---|---|---|
| K.. .. .. | 22·15 | — | — | 21·47 |
| Cr .. .. | 9·82 | 10·06 | 10·30 | 10·45 |
| $H_2O$ .. .. | 10·19 | — | — | 10·32 |

There can be little doubt that this is a salt of malonic acid analogous in composition to the corresponding oxalic acid compound. Like that body it is a dichroic—green and blue. Seen under the microscope, the crystals of the salt appear of a very fine green colour, or of a deep indigo blue colour, according to the axes along which the light is transmitted. The salt is green by daylight, but reddish blue by lamplight. The crystals are intensely coloured, so much so that only the thinnest crystals allow light to be transmitted, which by lamplight is of a reddish blue colour. The salt is very soluble in water, but insoluble in alcohol. When silver nitrate is added to a solution, a gelatinous precipitate of a reddish blue colour is obtained, which is the corresponding silver salt. This body is but slightly soluble in cold, but more soluble in hot water. The absorption-spectrum of the silver compound is the same as that of the potassium salt. Calcium chloride gives no precipitate when added to a solution of potassium chrom-malonate.

The crystals obtained by slow evaporation were larger, and were examined for their absorption-spectrum. It was found more convenient to mount them between glass, using Canadian balsam as a cement. The absorption-spectrum thus given was similar to that produced by crystals of the corresponding potassium chrom-oxalate.

The principal absorption-band in the red part of the spectrum is, however, noticeably darker and sharper. It is further remarkable as being distinctly nearer the blue end of the spectrum; and further, what frequently appeared as a shadow in former absorption-spectra, now appears in the case of this salt as a distinct band at 655. The absorption spectrum (10) of the crystals of this salt is as follows:—

A faint thin band at 714; a very dark and sharp band at 701. Then two faint bands at 681, and 660 respectively; further, another faint band at 655, which joins the broad

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* This and the other organic acids used were obtained from Kahlbaum, Berlin.

absorption ending at 507; and, lastly, continuous absorption from 465.

A solution of the salt in water is of a reddish blue colour and gives an absorption-spectrum exactly the same as that given by the crystal. The only difference is that the bands 681, 660, and 655 are less distant and less sharp.

When an excess of malonic acid is added to a solution of potassium chrom-malonate, two dark sharp bands are seen in the red part of the absorption-spectrum instead of one. These bands are slightly nearer the blue end of the spectrum as compared with those given by a solution of the salt $K_2Cr_2 4C_2O_4$, but in other respects the absorption-spectra are similar.

It would thus seem not unlikely that there is thus formed a compound of malonic acid analogous to the salt $K_2Cr_2 4C_2O_4$, but I have not succeeded in separating it.

Having now shown that there exists a double compound of potassium and chromium with malonic acid, analogous in composition, properties, and absorption-spectrum with the corresponding salt of oxalic acid, I naturally tried the next acid of the same series—succinic acid—by exactly the same method that enabled me to obtain the potassium chrom-malonate. I digested a portion of the specimen of chromium hydroxide which was used for making the malonic acid compound, and which was freshly precipitated with a solution of acid potassium succinate; the chromium hydroxide did not dissolve, nor was the solution in any way coloured. I then attempted to dissolve the chromium hydroxide in a concentrated aqueous solution of succinic acid. After prolonged heating a small quantity dissolved.* The solution had a green colour by daylight and a reddish colour by lamplight. It therefore differed in colour from the double salts which I had previously examined, and, as was to be expected, its absorption-spectrum was also different (12). It is characterised by having two dark bands 727—715 and 679—670 respectively. These absorption-bands are not so dark nor so sharp as the principal band in the red part of the spectrum given by the previously mentioned compounds of oxalic and malonic acids. Between these bands are two others, somewhat fainter but fairly sharp at 707 and 693 respectively. There is also another band at 655 which is rather difficult to see, as it is joined to the broad absorption which extends from 644 to 537, and, lastly, continuous absorption from 498.

The whole character of this absorption-spectrum is quite different from those previously described. It is more nearly related (as will be subsequently shown) to that given by the fatty acids when they are treated in the same way. I endeavoured to obtain a double salt in this case also, but my efforts were not successful, one reason being that the amount of chromium compound in solution was small.

(To be continued).

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## INSTRUCTIONS FOR THE EXAMINATION AND JUDICIAL DECISION ON PORTIONS OF ANIMAL ORGANISMS INTENDED FOR HUMAN FOODS.†

By WILHELM EBER.

With death decompositions set in in parts of the animal body, when portions of freshly-slaughtered animals are poorer in colouring-matter than they are subsequently. The muscles on access of air take a fuller yellowish-red colour; the liver and kidneys become a darker brown under the same circumstances. All other parts take a more or less decided admixture with yellow, which is particularly intense in the case of cattle which have been pasturing. The reaction of animal matter shortly after slaughtering is alkaline, and in the muscles, on the occurrence of coagulation, it becomes amphoteric, or slightly acid; this is *simple acidification*. Portions of the animal body may then by the development and action of ferments and septic organism pass into *acid fermentation* or into putridity, or into mixed processes of these two typical kinds of decomposition. The acid fermentation in substances which are rich in carbohydrates (liver and muscles) connects itself with simple acidification if sufficient moisture is present.

In large pieces of meat, suitably kept, it attains a high degree, and in its later stages it is characterised by the diminished power of the pigments of the muscles to assume a bright scarlet colour in contact with air. In the liver the dark brown pigment is changed by the acid fermentation to a light brown. The *rigor mortis* decreases under the influence of the acid fermentation, the meat becomes more tender and takes a pleasant acidulous odour. This process is called in lay circles "ripening," and the meat is said to have been "thoroughly killed."

In the subsequent stages of acid fermentation (fourteen days to three weeks) the muscular flesh, along with traces of hydrogen sulphide, contains a peculiar aromatic flavouring matter (haut goût). Haut goût is not a product of putrefaction.

Under especial conditions acid fermentation is accompanied by intensely stinking products. It is then called offensively *acid fermentation*. It occurs, *e.g.*, in the muscular tissues of game, which is dispatched in large quantities before it has lost its vital heat. The putrid products generally contain very much hydrogen sulphide. The pigment of the muscles assumes on the surface of fresh sections a colour from greyish green to leaf-green. Bubbles of gas may occur in the tissues.

Simple acidulation, acid and offensively acid fermentation, may be overpowered by true putrefaction. *Putrefaction is ammoniacal fermentation.* Free ammonia is always formed from albuminous and gelatigenous substances along with poisonous bases, fixed or volatile. The starting-point of putrefaction is the inter-muscular connective tissue. The true muscular fibre may, therefore, under some circumstances retain its acid reaction notwithstanding energetic putrefaction. Striking changes of colour appear only on those parts of hæmoglobiniferous objects which are exposed to the air and are by no means characteristic of putrefaction. Substances of putrid odour may be formed in putrescent substances, but are very often wanting (*e.g.*, in decomposing sausages). We must therefore discriminate between stinking and non-stinking putrefaction. For recognising putrefaction the author uses the alkaline reaction and tests for ammonia (see below).

The examination of meat is conducted as follows:—

1. The article is weighed, and if it has been refrigerated it is brought to the temperature of the room. We determine its form, the presence or absence of *rigor mortis*, and its state of nutrition.

2. Appearance of the free surfaces.

(*a*) The colour is observed in ordinary diffused light, in reflected light (lustre, phenomena of interference), and in the dark (phosphorescence). The transparence of the tissues is tested.

(*b*) Proportion of moisture, and if necessary coatings (mould adhesive paste). The colour of any coating upon a coloured ground can be determined only after a portion has been spread upon white paper.

(*c*) Odour: the decision should, if possible, be made by several persons. For demonstrating hydrogen sulphide a specimen of the object in question is put in a wine glass, the mouth of which is covered with a piece of white paper, on the under surface of which is placed a drop of solution of lead acetate. This drop is examined every five minutes (without raising the paper), and the obser-

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* The chromium hydroxide must be freshly precipitated, as on standing it quickly becomes insoluble in succinic and other weak acids.

† From the *Zeit. Anal. Chemie.*

vation is completed in fifteen minutes. The drop is coloured pale brown or black according to the quantity of hydrogen sulphide.

(*d*) The ammonia test, with at least five portions of the free surfaces. For this test the author uses two test glasses of equal width (having feet). One glass can be closed with a solid caoutchouc stopper, and the other with a perforated stopper of the same material. The perforation admits a glass rod, which projects into it beyond the middle of the test-glass.

Each of these glasses is charged to the depth of 1 c.m. with the following reagent:—Pure hydrochloric acid one part, three parts alcohol at 96 per cent, one part ether. Pure hydrochloric acid forms a grey mist even with watery vapour, and is therefore not suitable for the detection of minute quantities of ammonia in moist bodies. The glasses are then closed with their stoppers, and the glass with the solid stopper is moved as if we wished to heat its contents over a flame. But the liquid must not be made to move more than 1 c.m. above its original level. The glass is thus filled with the colourless vapours of the mixture of $HCl$, alcohol, and ether. Small quantities of the substance under examination are then peeled or scraped off and fixed on the glass rod of the perforated stopper. The solid stopper is then cautiously twisted out of the test-glass, and the charged glass rod is immersed in the test-glass so as not to soil the sides of the latter, and the portion of meat remains at the distance of from 1 to 2 c.m. from the surface of the liquid.

If no clouds appear—which is best observed if the glass is viewed against a dark background with the light from above—there is no ammonia present, and consequently no putrefaction. In presence of ammonia in all cases grey, smoke-blue, or white mists descend from the object to the surface of the liquid after having at first enshrouded the specimen. After the observation has been completed, the stopper with the rod is removed and the solid rod is re-inserted.

(To be continued).

# A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

## First Paper: The Analysis of Baric Bromide.

By THEODORE WILLIAM RICHARDS.

### *Introduction.*

In the course of a recent determination of the atomic weight of copper (*Proc. A. A. A. S.*, xxvi., 258), there was an attempt made to determine the ratio of cupric to baric sulphate; but in the discussion of the result it became evident that the ordinary method of precipitation was far too crude for the desired purpose. Moreover, even had there not been possible errors of a serious nature in the method, the atomic weight of barium was evidently too uncertain to form the basis of any accurate comparison. Hence this attempt was at the time given up, and the plausibility of the single result obtained was ascribed to a chance elimination of opposite errors.

During the early part of this century, a number of chemists have investigated the atomic weight of barium with very widely varying results. The first experiments worthy of mention were made by Berzelius and Klaproth (see Wollaston, *Phil. Trans.*, 1814, p. 20), but these are now of historical interest only. In 1818 the problem was again undertaken by Berzelius (*Pogg. Ann.*, viii., 189), who found that from 100·00 parts of anhydrous baric chloride he could obtain 138·07 parts of argentic chloride, whence the atomic weight is readily computed to be 136·8. At the same time he found that the same amount of baric chloride yielded 112·175 parts of baric sulphate, which gives Ba = 135·6.

In 1829 Edward Turner (*Phil. Trans.*, 1829, p. 296), published a re-determination of the latter ratio, finding the equivalents to be as 100·00 : 112·19. He, too, weighed the argentic chloride obtainable from a given amount of baric chloride, and arrived at the conclusion that the atomic weight of barium could not be far from 137·45. Two years later T. Thomson ("System of Chemistry," 7th Edition, 1831, I., 426) described several attempts to weigh barium as the sulphate, which need not be further discussed. In 1833 Turner (*Phil. Trans.*, 1833, p. 538) found as a mean of three experiments that 112·03 parts of baric nitrate were required to form 100·00 parts of baric sulphate,—a result indicating 137·0 as the atomic weight of barium. Ten years later Salvetat (*Comptes Rendus*, xvii., 318) published a very incomplete account of the quantitative study of the conversion of baric carbonate into sulphate, giving a final result of 136.

Soon after this both Pelouze (*Ibid.*, xx., 1047) and Marignac (*Liebig's Annalen*, 1848, lxviii., 215) determined the ratio of baric chloride to metallic silver, the first finding the atomic weight of barium to be 137·3, and the second 137·1. In 1850 Levol (*Ann. Chim. Phys.*, [3], xxx., 359) reduced auric chloride with sulphurous anhydride, and determined the sulphuric acid which resulted with baric chloride. Re-calculated with the recently determined atomic weight of gold, 197·3 (Krüss, 1887; Thorpe and Laurie, 1887; and Mallet, 1889), these results give 138·3 as the atomic weight of barium. In the next year H. Struve (*Liebig's Annalen*, 1851, lxxx., 204) found that 100 parts of baric chloride produced 112·094 parts of baric sulphate,—a value which leads to an atomic weight of barium equal to 137·0. T. Andrews (British Association Report, 1852, Part II., p. 33) obtained in 1852 the value 137·6, but he gives none of his details. Six years afterwards Marignac (*Liebig's Annalen*, cvi., 165) re-determined the ratio of baric chloride to the sulphate, with a result very different from those of his predecessors. In his hands 100 parts of the former salt yielded only 112·011 parts of the latter, instead of 112·09 or more. In the same investigation he determined the amount of water of crystallisation in baric chloride, with results so unsatisfactory that the values calculated from the various ratios varied from 128·5 to over 138 (see Meyer and Seubert's "Atomgewichte," p. 176), as well as the ratio of baric chloride to metallic silver. This last determination led to a value for barium only four $\frac{1}{100}$ths of a unit higher than his previous work ten years before. He admits that the substances used in the analysis were not perfectly pure, but assumes that the impurities were not great enough seriously to influence the result. At about the same time Dumas (*Liebig's Annalen*, cxiii., 22) was also determining the ratio of baric chloride to silver. He fused the salt in a stream of hydrochloric acid gas, but gives no proof that a slight excess of the gas was not absorbed. If this had been the case, of course the observed atomic weight of barium would have been too low. As a matter of fact, he obtained 137·0 for the value of this "apparently variable constant." Below is tabulated a list of the various determinations, grouped according to the processes employed.

*The Atomic Weight of Barium.**

O = 16·000.

Analysis of baric carbonate :—

| | |
|---|---|
| Berzelius, 1811 .. .. .. | Ba = 134 to 143 |
| Wollaston and Klaproth, 1814 .. .. | 139·2 |
| Salvetat, 1843 .. .. .. .. .. .. | 136 |

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* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

* The writer is much indebted to the works of Becker, Clarke, Meyer and Seubert, and Ostwald for valuable assistance in preparing this list.

Conversion of baric chloride to sulphate:

| | |
|---|---|
| Berzelius, 1818 | Ba=135·6 |
| Turner, 1829 | Ba=135·4 |
| Thomson, 1831 | Ba=136± |
| Struve, 1851 | Ba=137·0 |
| Marignac, 1858 | Ba=138·5 |

Conversion of nitrate into sulphate:

| | |
|---|---|
| Turner, 1833 | Ba=137·0 |

Comparison of baric sulphate with gold:

| | |
|---|---|
| Levol, 1850 | 138·3 |

Ratio of baric chloride to argentic chloride:

| | |
|---|---|
| Thomson | Ba=136± |
| Berzelius, 1818 | Ba=136·8 |
| Turner, 1829 | Ba=137·4 |
| Marignac, 1858 | Ba=137·1 |

Ratio of baric chloride to silver:

| | |
|---|---|
| Pelouze, 1845 | 137·28 |
| Marignac, 1848 | 137·11 |
| „ 1858 | 137·15 |
| Dumas, 1859 | 137·00 |

Ratios including water of crystallisation:

| | |
|---|---|
| Marignac, 1858 (averages) | 130·7 to 138·5 |

Unknown ratio:

| | |
|---|---|
| Andrews, 1852 | 137·6 |
| Clarke, 1883, selects* | Ba=137·0 |
| L. Meyer and Seubert, 1883, select | Ba=137·2 |
| Ostwald, 1885, selects | Ba=137·04 |
| Van der Plaats, 1886, selects | Ba=137·1 |

A cursory glance at the list will show a lamentable lack of consistency in the results of even a single method in different hands. The only ratio which seemed capable of yielding approximate results was the ratio of baric chloride to metallic silver, and here the variations in the atomic weight of barium amounted to nearly three-tenths of a unit. The question whether the errors were due to mechanical defects of analysis, or to admixture of foreign substances, became an important subject for consideration; but it is evidently of little use to re-calculate such heterogeneous results. The necessity for a careful experimental revision is very apparent. Such a revision would be especially interesting in view of the fact that barium is a member of one of the best marked series of elements known,—a series which might yield important information regarding a possible mathematical relation of the atomic weights. Moreover, the atomic weights of no less than eighteen other elements† have been determined, at one time or another, by reference to baric sulphate. Most of these determinations have been made without the least precaution with regard to the baric chloride occluded in the precipitated sulphate, or on account of the solubility of the sulphate itself; but even if the method had been satisfactory, the determinations could not be considered as anything more than crude approximations, because of our uncertainty regarding the molecular weight of baric sulphate.

These were some of the considerations which prompted the present undertaking. It is not unnatural that the revision should have been begun with the more or less strong belief that the atomic weight of barium could not be far from 137·1; but the progress of the work has completely overthrown this belief, and has indicated a much higher value.

(To be continued).

**Mica.**—Messrs. Wiggins and Sons have again obtained the Admiralty contract for the supply of Mica.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, April 20th, 1893.*

Dr. Armstrong, President, in the Chair.

Mr. Wm. E. Wheeler was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Bailey, 18, Lavender Sweep, London; Douglas S. P. Berringer, B.A., Malvern College, Malvern; John Henry Coste, 69, Goswell Road, E.C.; Arthur Henry Green, 176, Lloyd Street, Greenheys, Manchester; Charles Mills, Hazeldean, Fulham Park Gardens, S.W.; Alexander Orr, 109, Pitt Street, Sydney, Australia; Charles Herbert Pring, The Ferns, Longfield Road, Bristol; George Ritchie, 8, Buchanan Gardens, Mount Vernon, N.B.; Henry Thomas Sorrell, Holly Lodge, Hill, Southampton West; Sydney Whalley, 38, Havelock Street, Canterbury; Thomas Whittaker, 76, Arden Terrace, Accrington.

Of the following papers those marked * were read:—

*1. "*A Contribution to the Chemistry and Physiology of Foliage Leaves.*" By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D.

The investigation relates to the occurrence, relations, and physiological significance of the starch, diastase, and sugars contained in foliage leaves.

The authors divide the subject into two parts; the first, dealing with the starch and diastase of leaves, is subdivided into the following sections:—(1) Introduction; (2) Historical; (3) The Starch of the Leaf, its Determination, and the Proportion it bears to the Total Products of Assimilation; (4) The Occurrence of Diastase in the Leaf; (5) The Nature of the Products of Transformation of Starch by Leaf-Diastase; (6) The Determination of the Diastatic Activity of Leaves; (7) The Periodic Variation of the Diastase of Leaves; (8) Can Leaf-Diastase Act on Solid Starch? (9) How Far is the Disappearance of Leaf-Starch due to Living Protoplasm? The second part treats of the sugars of the leaf, and consists of an historical section, and one dealing with the sugars of *Tropœolum majus*. The bibliography of the subject is summarised in an appendix.

The work originated in an attempt to discover the explanation of the conditioning effect of "dry-hopping," *i.e.*, the addition to finished beer of a small amount of dry hops. This was ultimately traced to the presence in the hop-strobiles of a small, but appreciable, amount of *diastase*, sufficient to slowly hydrolyse the non-crystallisable products of starch transformation left in the beer, and to reduce them to a condition in which they can be fermented by the yeast. In endeavouring to ascertain if this occurrence of diastase in the hop-strobile was an isolated case, or a special example of a widely distributed property of vegetable tissue, the authors were led to enquire into the first formation of starch in the chloroplasts of the foliage leaf, the mode of its dissolution and translocation in the plant, and the nature of the metabolised products.

The results obtained are regarded as entirely antagonistic to the assumption made by Sachs, that all the products of assimilation at some time take the form of starch.

Using the half-leaf gravimetric method devised by Sachs, the authors confirm his results as to the rate of assimilation, but they show that only a small portion of this assimilated material exists at any one time in the form of *starch*.

The starch in leaves was estimated by hydrolysing it, with suitable precautions, with the aid of diastase, and then determining the products of its hydrolysis in the

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* In Clarke's original treatise 137·007 is apparently misprinted for 137·07 (Smithsonian Misc. Coll., vol. xxvii., p. 63).

† Li, Be, F, Mg, Si, V, Cr, Ni, Cu, Se, Y, In, (Ba), La, Ce, Di, Au, Tl, Th.—Compare L. Meyer and Seubert's "Atomgewichte," p. 105.

usual way by means of the polarimeter and Fehling's solution. The fluctuations in the amount of starch in leaves under various conditions, and also in leaves plucked at different times in the day, have been determined by this method.

It is shown that Wortman's recent denial that diastase plays any part in the dissolution and translocation of starch in leaves is incorrect. The authors prove that, instead of leaves containing little or no diastase, every leaf examined by them contained sufficient diastase to transform far more starch than the leaf can have contained at any one time; in many cases sufficient diastase was present to hydrolyse an amount of starch many times the total dry weight of the leaf. The difference between the authors' and Wortmann's results is chiefly due to the fact that whereas Wortmann examined the clear filtrate obtained by macerating the crushed leaves in water during a few hours, they have digested the air-dried and powdered leaf itself with soluble starch solution.

It is further shown that the products of the hydrolysis of starch by leaf diastase are identical with those formed by malt diastase, maltose having been directly separated from the leaves, and its optical and reducing properties determined. Leaf diastase is not able to convert maltose into dextrose, but the leaf contains an enzyme capable of inverting cane-sugar.

In the course of a large numbei of comparative determinations of the diastatic activity of various leaves, it was found that the amount of diastase varied greatly in different plants, and within narrower limits even in the same plant at different times. It is very high in the case of the Leguminosæ, the diastatic activity of *Pisum sativum* being between one-half and one-third of that of an average pale barley malt.

An attempt to ascertain if the fluctuations in diastase were in any way periodic, or were governed, as are the fluctuations of starch in the leaf, by any external conditions, showed that any conditions which favour a decrease in the leaf starch result in an increase of the leaf diastase; for instance, leaves kept in darkness, either on or apart from the plant, show a marked increase in diastatic activity. In view of the results obtained in their former paper on the "Germination of the Gramineæ" (*Trans.*, 1890, 458), the authors explain this by the assumption that as long as the conditions favour assimilation, the leaf cells are necessarily supplied with an abundance of newly assimilated materials in the form of sugars, more, in fact, than can be easily made use of or translocated, the excess of nutritive material being in part deposited as starch. At this period there is little or no elaboration of diastase by the cell protoplasm, probably none at all in those cells in which starch deposition is actually going on. When the light fails and assimilation consequently falls off, the living cells speedily use up or translocate the excess of assimilated products, such as cane-sugar, and begin to draw their supplies from the more permanent starch. To enable the cells to do this effectually, the somewhat starved protoplasm now commences to elaborate the needed diastase more rapidly, and the secretion of the enzyme becomes accelerated as the starvation point of the cell is reached, the secretion of diastase by the leaf cell being, in fact, like that of the embryo of the grasses, to some extent a *phenomenon of starvation*. Experiments confirmed this view.

Contrary to Wortmann's statement, it was found that under certain conditions leaf diastase can attack the solid starch granule; but attempts to obtain any evidence of the disappearance under the influence of the contained diastase of starch in killed leaves gave negative results, and the authors are led to the conclusion that the *first stage* of dissolution of the starch granule in the leaf is in some way or other bound up with the *life* of the cell. When, however, all the facts are considered and due weight given to (1) the constant and abundant occurrence of diastase in leaves, (2) to the apparent correlation of this diastase with the occurrence of starch, (3) to the remarkable periodicity of the rise and fall of diastase, and (4) to the correlation of this periodicity with the appearance and disappearance of starch, it is impossible to accept Wortmann's view that the dissolution of starch in the leaf is in no way conditioned by a starch-dissolving enzyme. On the contrary, the authors believe that their experiments establish beyond all doubt the physiological importance of diastase as an active agent in the dissolution and translocation of starch, not only in leaves, but also in the growing parts of all plants. As further evidence of this, the authors adduce the fact that *maltose* was found amongst the sugars of the leaf when the starch was disappearing.

Selecting the leaves of *Tropæolum*, experiments were carried out to ascertain the nature of the leaf sugars and the variations in amount and relative proportions at different times, and also for the purpose of throwing some light on the relation which each sugar bears to the primary assimilation products on the one hand, and to the leaf starch on the other, *i.e.*, to ascertain which are the true "up grade" sugars from which starch is formed, and which are the "down grade" sugars resulting from the hydrolysis of starch.

The only sugars found were *cane-sugar*, *dextrose*, *levulose*, and *maltose*. The total amount of the sugars is subject to great variations, and the relative proportion which they bear to each other is also very varied. The results obtained lead to the following conclusions:—Cane-sugar is the first sugar to be synthesised by the assimilatory processes. This sugar accumulates in the cell sap of the leaf parenchyma when assimilation is proceeding vigorously, and when the concentration exceeds a certain point starch commences to be elaborated by the chloroplasts at the expense of the cane sugar. This starch forms a more stable reserve material than the cane-sugar, and is only drawn on when the latter more readily metabolised substance has been partially used up. Cane-sugar is translocated as dextrose and levulose, and the starch as maltose. From the invert sugar derived from the cane sugar, the dextrose is more readily used up for the respiratory processes, and possibly also for the new tissue building, than is the levulose; hence in a given time more levulose than dextrose must pass out of the leaf into the stem.

### Discussion.

The President, after remarking that a more suggestive paper had never been brought under the notice of the Society, referred to the statement made by the authors regarding the oiigin of the research as a striking illustration of the advantage to be derived from the association with our manufacturing industries of thoroughly qualified scientific men. A research originally commenced with the object of explaining a common brewery practice had not only afforded the required information, but in addition improved methods of analysis had been devised in the course of the work; and facts had been discovered which ultimately might serve as the basis for the interpretation of the manifold changes involved in the formation and degradation of carbohydrates in plants, and which also might largely contribute to the solution of purely theoretical problems concerning the nature of the carbohydrates. He was not prepared to allow the interpretation of the manner in which cane-sugar was formed that had been put forward by Messrs. Brown and Morris to pass unchallenged. On a previous occasion, when discussing their paper on the "Germination of the Gramineæ," he had suggested that perhaps cane-sugar was formed from maltose, and not from dextrose and levulose, to unite which all attempts hitherto made had failed; that, in fact, one of the dextrose residues of maltose was converted into levulose, and that the compound thus formed underwent a change—an internal condensation—resulting in the production of cane-sugar, the nature of which even yet is not understood, but which, apparently, does not contain aldehydic groups. The evidence now brought forward was, he thought, compatible with this view.

Such a passage from maltose to cane-sugar would be of advantage to the plant, as it would then have at disposal a material that was hydrolysed more easily than maltose; the superior nutritive value of cane-sugar might be due at least partly to this fact. Levulose perhaps played a special part in certain metabolic processes; it was well known to be much more sensitive than dextrose towards hydrolytic agents, the formation of levulinic acid being an instance of this, and it was not improbable that it was therefore of superior value in comparison with dextrose and other carbohydrates, because able to take part in some of the changes involved in the elaboration of tissue to which other carbohydrates, on account of their stability, were at least less readily amenable.

Mr. Thiselton Dyer said that he was much mistaken if this paper did not prove to be one of the most important contributions to the study of plant metabolism of the century. The problems involved are open to two lines of attack, the botanical and the chemical: neither, in his opinion, could lead to wholly satisfactory results. It was Mr. Horace Brown's singular merit that he had been able to combine both; his conclusions may therefore be expected to be convincing both to the botanist and to the chemist.

It was not too much to say that botanists have long waited for the work which Mr. Horace Brown and his colleague are doing and have done. A good many years ago Dr. Hugo Müller had pointed out to him how far in advance in these matters the botanical results were of those which chemists had reached. And to a botanist not the least interesting feature in this paper was the frank recognition of the value, from a chemical point of view, of the classical work accomplished in this field by Sachs and Schimper. The botanical attack had for the time, however, gone as far as it could, and it awaited the chemical complement which it is now in a fair way to receive.

The primary fact of plant "assimilation" is assumed. That is an outcome of protoplasm activity, the details of which we need not discuss. The result is generally admitted to be what we may call a "proto-carbohydrate." Now this substance reveals itself in a visible and derivative form, on the one hand in cellulose and on the other in starch. The deposition of the former is the work of the general protoplasmic body of the cell; that of the latter is, as far as we know, the special function of certain specialised protoplasmic corpuscles, known as plastids. Of these, botanists now recognise three separate groups —chloroplastids, chromoplastids, and leucoplastids. The latter are identical with the amyloplasts of Schimper. We now have reason to believe that these groups may be reduced to two—the coloured and the colourless plastids; the chloroplastids in point of fact are only a particular phase of the chromoplastids. All alike possess the common property of determining the formation of "starch granules." The more we know of these bodies the more remarkable are their properties; they appear to have their own independent method of multiplication by division; it is even probable that they are bodily inherited from one plant generation to another; and both Schimper and Lankester have hinted that they may be autonomous organisms leading a commensal existence with the plant whose physiological needs they so conspicuously subserve.

Nothing is so remarkable in the general survey of plant metabolism as the repeated passage of its products from the soluble to the insoluble form, and *vice versâ*. He had long been of opinion that the key to the *modus operandi* of these transformations is to be found in the action of enzymes, and had done his best to emphasise the view in an address which he gave to the British Association in 1888. But in science a merely theoretical view is of little value without a formal proof. And as regards the mode in which starch is brought into use, it appeared to him that Mr. Horace Brown had for ever set that question at rest. The difficulties raised by Wortmann never weighed much with botanists, and Mr. Horace Brown had demolished them, as it seemed to him, for ever.

So far we were very grateful to the authors of the paper for clearing the way for us. But what follows was not, at present, free from difficulty. The botanical point of view was briefly stated by Sachs in the case of the sugar beet: starch in the leaf, glucose in the petiole, cane-sugar in the root. As he had pointed out in the *Kew Bulletin* for 1891, the facts in the sugar-cane seem to be strictly comparable. Cane-sugar the botanist looks on, therefore, as a "reserve material." He had ventured, in fact, to call "glucose" the sugar "currency" of the plant, cane-sugar its "banking reserve."

The immediate result of the diastatic transformation of starch is not glucose, but maltose. But Mr. Horace Brown had shown in his remarkable experiments on feeding barley embryos that, while they can readily convert maltose into cane-sugar, they altogether fail to do so with glucose. We may conclude, therefore, that glucose is, from the point of view of vegetable nutrition, a somewhat inert body. On the other hand, evidence is apparently wanting, that maltose plays the part in vegetable metabolism that might be expected of it. Its conversion into glucose may be perhaps accounted for by the constant presence in plant tissues of vegetable acids. But, so far, the change would seem to be positively disadvantageous. Perhaps glucose, in the botanical sense, will prove not to have a very exact chemical connotation.

That the connection between cane-sugar and starch is intimate is a conclusion to which both the chemical and the botanical evidence seems to point. And on botanical grounds this would seem to be equally true of its connection with cellulose.

It must be confessed, that the conclusion that "cane-sugar" is the first sugar to be synthesised by the assimilatory processes is one which is rather startling to the botanist. It seems hard to reconcile with its probable high chemical complexity and with the fact that, botanically, it seems to stand at the end and not at the beginning of the series of metabolic change.

A few words must be said, in conclusion, on the references made by Mr. Horace Brown to the part played by protoplasm.

"Protoplasmic continuity" is a great induction, to the establishment of which the work accomplished by Mr. Gardiner at Kew had, in great measure, contributed. He was, however, inclined to approach with caution the use Mr. Horace Brown had made of it. He was far, himself, from thinking that it can at present be relied on to explain the "rapid translocations" of metabolites. For his part, for various reasons, he had been content to think that, where a tract of tissue becomes the seat of an enzymic action (as in germination), the continuous protoplasm may act as the means of transmission of an enzyme from cell to cell, or even of some influence by which an enzyme is set free from a zymogen. But he doubted the evidence at present being sufficient to accept it as the path of the bodily transmission of a metabolite.

The resistance which living protoplasm presents to the ordinary physical processes of diffusion is an old difficulty. Invoking the continuity of protoplasm did not in his opinion materially dispose of it. But, on the other hand, it must be remembered that the cell, which is the active seat of metabolic change, is in a state of tension; and the opposition offered by protoplasm to diffusion is mitigated by the fact that it cannot be invariably regarded as a continuous membrane, but is itself, under such circumstances, frequently porous and subject to physical permeability.

He must finally relieve his mind of an idea that had often occurred to him about protoplasm as the seat of chemical changes of immense importance. In the laboratory we are accustomed to deal with organic substances as comparatively stable. Their molecular up-building or synthesis, when effected by the chemist, is generally difficult and circuitous. He thought we must accustom our minds to the fact that in the "protoplasmic field" these processes may be much more easily accomplished. Under such circumstances it appeared to him that the molecules of various substances may be subject to soliciting influences of the nature, perhaps, of solution, which, without altering their chemical identity or constitution, may make their chemical transformation far more easy to accomplish than it is by ordinary chemical means. He was not desirous of violating chemical order or law, or of claiming for protoplasm any "vitalistic" properties, but at the same time it would be absurd to shut our eyes to the unique properties that protoplasm possesses, or to refuse to admit that it may, in consequence, have the power of conditioning chemical change in a probably unique manner. At any rate he might point to the facility with which, in the field of organic nature, chemical change seems to be effected, and to the profusion of products which result from it. What nature, with the aid of protoplasm, appears able to effect with extreme facility the chemist can only follow with laborious difficulty.

No doubt it may be said that this is to introduce a new and unknown quantity into chemistry—a biological element, in fact. Why not? He could conceive that the path of chemical change in the organism may be conditioned by adaptive requirements, by natural selection in fact, and that the substances which now dominate the chemistry of plant life may have attained their prominence, not so much in obedience to unselective chemical change as to the requirements of plant life. Enzymes, for example, may, in the first place, have been mere proteid derivatives of protoplasm. But their peculiar properties of bringing about fermentative change may have rendered possible, and, therefore, stereotyped, the whole series of plant metabolism, with its singular alternation of soluble and insoluble products.

Dr. D. H. Scott said that since the publication of Schimper's paper of 1885, the idea that starch is not the first product of assimilation had been familiar to botanists. In fact, Sachs himself had never said that it was so, but had spoken of starch as the first *easily demonstrable* product. Botanists generally supposed, with Schimper, that glucose, or some similar sugar, is a prior product to starch. Messrs. Brown and Morris's conclusion that cane-sugar is first formed was an entirely new departure.

The paper proved that the starch formed by the chloroplasts is precisely the same thing as starch formed by leucoplasts, namely, a reserve food substance, and nothing more. So far, the chloroplast is physiologically as well as morphologically identical with an amyloplast destitute of chlorophyll. But the chloroplast has the further, quite distinct, function of forming a carbohydrate in the first instance from inorganic materials.

Messrs. Brown and Morris had shown what brilliant results might be attained when skilled chemists devoted themselves to physiological problems.

Professor Green, after alluding to the author's theory of the improbability of all the carbonaceous material of the plants' food passing through the starch stage, referred to the possibility that at the same time that the formation of carbohydrate was taking place there might be a coincident formation of vegetable acids, part of the increase in weight of the leaf being so accounted for; thus from formaldehyd it seemed possible to pass to formic acid, and subsequently to higher acids such as the parenchyma of the plant contains.

He asked also whether in noticing the variation of the diastatic power of the leaf at different times of the day the author's attention had been directed to a possible inhibitory effect of light upon its action. The quantity might vary as the author suggested, but it was at least possible that with a constant quantity the diastatic action might be much less in the daytime, owing to the diastase being unable to work in sunlight.

In this connection Professor Marshall Ward's experiments on the bactericidal action of certain rays were significant, as they indicated a possibility of protoplasm being directly affected by these rays. If protoplasm itself is so interfered with, might not its enzymes also be disturbed by the same influence?

The views of Böhm and Baranetzky as to the diastase being used up in course of its activity are not in accord with the opinion of most workers on the enzymes. As Mr. Brown appeared to endorse these views to a certain extent, could he quote experiments clearing up the point? O'Sullivan's experiments on invertase (*Chem. Soc. Trans.*, Oct., 1890) pointed to a directly opposite view.

In criticising Wortmann's method of preparing his extracts, Mr. Brown had pointed out the difficulty of extracting enzymes by water. There was another solvent which, in many cases, offered great advantages, viz., a 5 per cent solution of common salt. The greater power of this as an extractive was possibly connected with the frequent association of the enzymes with globulins.

Dr. Lauder Brunton observed that the paper opened up very many new lines of inquiry. It threw a light not merely on vegetable physiology and chemistry, but on the physiology of animal life, and also on that of the lowest organisms which could hardly be reckoned either as animal or vegetable. He thought that perhaps animal life in its turn might throw a light on vegetable physiology, and instanced the close resemblance that existed between the storage of glycogen in the liver of animals during digestion, with its subsequent conversion into sugar, and the temporary accumulation of starch and its subsequent removal from the leaves of plants. In the pancreas of an animal, one of the enzymes which was present in the juice of the secreting gland and also in its substance appeared to be entirely absent from the gland of fasting animals. This absence is only apparent, for the enzyme is really present, not in an active condition, but in the form of a zymogen. From this zymogen the active enzyme may be liberated by treatment with dilute chlorhydric acid and subsequent neutralisation. He was desirous to know whether any such zymogen had been found in leaves where starch was accumulating. The pancreas of animals was also remarkable in this particular, that while the gland was pouring into the intestines a juice which converts starch into sugar, it was also pouring through the lymphatics into the blood an enzyme which destroys sugar. He thought it possible that more than one enzyme might be present in the leaves of plants, and was anxious to know whether any observation had been made as to the presence of an enzyme in the plant which could decompose sugars.

(To be continued.)

## PHYSICAL SOCIETY.

*Ordinary Meeting, April 28th, 1893.*

Prof. W. E. Ayrton, F.R.S., Past President, in the Chair.

Mr. F. Harrison was elected a member of the Society.

Adjourned discussion on "*The Viscosity of Liquids*" by Prof. J. Perry, J. Graham, and L. W. Heath.

Prof. Perry read a communication he had received from Prof. Maurice Fitzgerald on the subject, in which the latter discussed the corrections necessary for reducing the results obtained by circular motion to the corresponding motion in plane layers. He shows that in addition to the circular motion, the effect is complicated by radial flow, due to "centrifugal head," which causes the liquid to pass outwards near the bottom of the trough, and inwards across the edge of the suspended cylinder, with continuations along the sides of the trough and cylinder. Taking this motion into account, the formula—

$$v = \mathrm{A}r^{1+\frac{c}{\mu}} + \frac{\mathrm{B}}{r}$$

is deduced, where $v$ is the velocity, $\mu$ the viscosity, A and B arbitrary constants, and $c$ a constant depending on the radial flow. When $c = 0$ the formula reduces to equation (5) of the paper, whilst if $c = -2\mu$ it becomes—

$$v = \frac{C}{r}.$$

The subject of critical velocities in non-turbulent motion is referred to, and some probable effects of the anomalous variations of density and viscosity of sperm-oil noticed by the authors of the paper are pointed out.

Prof. **Perry**, in further reply to Prof. Osborne Reynolds' comments, said he understood Prof. Reynolds to have proved that friction was proportional to velocity when the motion was steady. Experiments he (Prof. Perry) had made with discs of iron and glass in revolving mercury seemed to show that this was not the case. On replacing the mercury by sperm-oil he found that up to a certain speed friction was strictly proportional to velocity, whilst above that speed friction varied as $v^{1\cdot25}$. Coloured streaks in the liquid remained unbroken even at the highest speeds. He therefore concluded that continuity of the streaks was not necessarily accompanied by a linear law of friction.

Mr. E. C. **Rimington** read a paper on "*Luminous Discharges in Electrodeless Vacuum-Tubes.*"

The luminous rings produced in exhausted bulbs and tubes by discharging Leyden jars through coils surrounding them had, he said, been attributed by Mr. Tesla (*Electrical Engineer* of New York, July 1, 1891), to the electrostatic action of the surrounding wire rather than to the rapidly varying magnetic induction through the rarefied gas. The present paper describes several experiments bearing on this point, which leads the author to conclude that varying magnetic induction is the chief cause of the luminous rings. They also show that a superposed electrostatic field greatly assists the production of the luminosity. Most of the experiments described were performed before the meeting, some of the effects being particularly brilliant. In one experiment an exhausted bulb was placed within a coil connecting the outside coatings of two Leyden jars, and placed between two metal plates which could be connected at will with the outside of either jar. The spark gap between the inner coatings was then arranged so that no luminosity was seen in the bulb. On connecting one or both the metal plates with the jars in such a way as to increase the electrostatic field through the bulb, bright rings immediately appeared. An electrostatic field produced by a small induction coil connected to a piece of tin foil on the bulb caused the rings to form at irregular intervals when the discharge of the jars and coil happened to be properly timed. In another experiment two loops of wire in series were used, and when put on the bulb in such a way as to produce a large magnetic effect but small electrostatic field, bright rings appeared; but if the magnetic effects of the coils opposed each other, whilst the electrostatic field was increased, no rings were seen. The subject is treated mathematically at some length in the paper, the times at which the maximum values of the current—the potential difference between the outsides of the jars and the rate of change of current—occur, as well as the values of their successive maxima being determined. The influence of "size of jars" is next considered, and the time integral of rate of change of current on which the effect on the eye depends expressed as a geometrical series. Taking an approximation, the author shows that the time integral is roughly proportional to the fourth root of the capacity. Large jars are therefore theoretically only slightly better than small ones, and this agrees with observation.

On the subject of "apparently unclosed discharges," such as are seen when discharges pass through a coarse spiral wound on an exhausted tube, the author said he had observed that the discharges were really closed, but the return part was much diffused and of feeble intensity. Experiments were exhibited showing that under some circumstances an exhausted bulb acted like a closed metallic circuit, whilst under other conditions dissimilar effects were produced. Another experiment was shown in which a faint luminous ring produced by a single turn of insulated wire round a bulb, was apparently repelled on touching the wire with the finger. The author also showed that fan-shaped luminosities could be produced by rotating an exhausted tube in the electrostatic field produced by a charged ebonite or glass rod.

Dr. **Sumpner**, speaking of the apparently unclosed discharges, pointed out that they might be closed through the wire forming the primary circuit in the same way as a coil of a transformer might be arranged to act, partly as primary and partly as secondary.

Mr. A. P. **Trotter**, after referring to Dr. Bottomley's researches, said it was important in discussing such experiments to distinguish between electrostatic and electromagnetic effects. In Mr. Campbell Swinton's experiments the luminosity always appeared to get as far away from the wire as possible, and to be at right angles to it; whereas in Mr. Rimington's the luminous portions were close to the wire. With a view to puzzling the discharge in Mr. Swinton's tubes, he had made a right angled bend in the spiral surrounding the tube, the result of which was to make the luminosity discontinuous, one end of the break being bifurcated. In all Mr. Swinton's experiments brush discharges surrounded the wire.

Prof. S. P. **Thompson** thought an electrostatic field would aid a discharge even if its direction was not the same as the E.M.F. due to varying magnetic induction. Planté had found that vacuum-tubes through which 800 cells were insufficient to produce a discharge, immediately allowed a discharge to pass when a rubbed ebonite rod was brought within about ten feet distance. This effect was found to be independent of the direction of the disturbing field. Analogous effects had also been observed by Prof. Schuster, and described in his Bakerian Lecture.

Mr. E. W. **Smith** regarded the stresses set up in the medium as cumulative, a very slight cause acting on a substance already strained nearly to breaking-point being sufficient to cause breakdown.

Mr. **Blakesley** inquired if the effects were the same if the induction-coil used in one of the experiments was replaced by an electric machine, and whether the direction of the field so produced influenced the result.

Mr. W. R. **Pidgeon** said closed circuits were necessary; he had found it very difficult to produce discharges in tubes unless the ends of the primary wire were brought together.

In his reply, Mr. **Rimington** said each turn of the luminous spiral formed a complete circuit of itself. The phenomena observed by Mr. Campbell Swinton were quite different to those he had shown and due to different causes. Mr. Swinton's spirals were reversed, and were due to phosphorescence of the glass.

## NOTICES OF BOOKS.

*A Manual of Dyeing.* For the Use of Practical Dyers, Manufacturers, Students, and all interested in the Art of Dyeing. By **Edmund Knecht**, Ph.D., F.I.C., Head of Chemistry and Dyeing Department of the Municipal Technical School, Manchester; Editor of the *Journal of the Society of Dyers and Colourists*; **Christopher Rawson**, F.I.C., F.C.S., late Head of the Chemistry and Dyeing Department of the Technical College, Bradford; Member of Council of the Society of Dyers and Colourists; and **Richard Loewenthal**, Ph.D. With numerous Illustrations and Specimens of Dyed Fabrics. Two vols., 8vo., pp. 907, and a Third vol. of Dyed Patterns. London: Charles Griffin and Co., Lim.

Of all the departments of chemical industry none have probably undergone a change so complete as the tinctorial arts. It is not too much to say that an experienced dyer—at once practical and theoretical—of the middle of the present century would be no little puzzled could he take up these volumes and glance through their contents. He would not merely encounter a host of new dye-wares and miss his old familiar friends, or at least find their relative importance greatly diminished, but he would encounter new principles. In place of the long lists of recipes he would find his attention called to the underlying conditions. Here it is that the dyer of the old school often went astray. As long as he had the same water, the same wares, and the same growth, say, of wool year by year, he could produce excellent work; but place him amidst new conditions and he felt lost. But the dyer of the new school, if properly trained, knows how to accommodate himself to varying circumstances.

The rival theories of the process of dyeing are duly expounded. The balance of evidence seems now to turn more and more in favour of the chemical theory. The chemical character of cellulose is carefully studied. A curious fact is the obstinacy with which Mercer's great invention has been and is still disregarded, although a French company, as we are told, offered him the sum of £40,000 for his patent rights.

As the average proportion of moisture in wool is no less than 18·25 per cent, it is interesting to learn that, following the example of the chief industrial countries abroad, a "conditioning house" has been established at Bradford in which the moisture of wools sold is officially tested.

The moisture in manufactured woollen goods, *e.g.*, blankets, is not to our knowledge under any official control. Hygroscopic substances are or have been employed by certain manufacturers for the purpose of increasing their weight.

Mention is here duly made of some of the injurious effects of the sulphur naturally present in wool. The comparative behaviour of wool and of silk with reagents is very fully and ably explained.

The authors judiciously advise that in localities where the ordinary water supply is hard, or otherwise impure, the owners of dye-works might with advantage pay more attention to the collection and storage of rain-water. The evils of hard and especially of ferruginous water are fully described.

It is stated that only one firm in England (Messrs. Ainsworth and Co., of Bolton) are using the Mather-Thompson bleaching-process, notwithstanding its demonstrated advantages. The electrolytic bleaching-process is not described.

In wool-bleaching, the use of stale urine (lant) is said to have been almost entirely superseded in England. Among the by-products of wool-washing, the potassium carbonate is said to be more valuable than the fatty matters. But in any case the suint and the fat from the soaps used in washing and milling must be recovered to avoid the pollution of the streams. The use of volatile liquids for wool-washing has not yet become general.

In bleaching wool and woollen goods sodium bisulphite and liquefied sulphur dioxide are coming into use, gaseous sulphurous acid (the old stoving process) being very injurious to the workmen. The use of hydrogen peroxide is restricted by its high price. It is a curious fact that for silk-bleaching neither sodium bisulphite nor liquefied sulphurous acid have proved satisfactory.

The preparation and properties of "alizarin oil" is discussed at some length and presents some unsettled points.

It is somewhat remarkable that in the very elaborate section on the tannins, though their use in "weighting" or "loading" silks is mentioned, yet the plainly fraudulent character of this process does not meet with a word of condemnation.

The section on mordants is fully on a level with present practice. Since the general introduction of the coal-tar colours, the importance of the tin mordants has greatly declined, and many preparations once highly valued have now little more than a historical importance. On the contrary, the antimonial mordants are coming more into use.

The recent enactment for the addition of coal-tar naphtha to methylated spirit,—thereby spoiling it for a number of purposes—is mentioned without criticism. If there was danger lest the spirit might be applied to non-technical uses, why was not a minute addition of Dippel's animal oil employed, as is the case in Germany?

In Part VI., which treats of the natural colouring-matters, we find the statement that in England the old law prohibiting the use of indigo has never been repealed! It is, of course, practically obsolete; but it might at any time be revived by an evil disposed person.

It is interesting to find that the part played in indigo-dyeing by a micro organism, *Desmobacterium hydrogeniferum*, is here fully recognised.

Is it not possible that improvements may be effected, *e.g.*, in the production of the weed-colours by the use of pure microbian cultures?

We hope to resume our notice of this most valuable work.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 17, April 24, 1893.

**New Researches on Micro-Organisms. Fixers of Nitrogen.**—M. Berthelot.—The author's experiments prove that there exist microbia of very different species, free from chlorophyll, and capable of fixing nitrogen, especially certain bacteria of the soil. It is seen that the nutrition of these plants does not appear capable of being maintained by the carbon and hydrogen resulting from the decomposition of the atmospheric $CO_2$ and $H_2O$. It is correlative with the destruction of certain hydrocarbons such as sugar or tartaric acid, which in some way act as foods for the bacteria and (other?) micro-organisms. For these beings to fix nitrogen it is necessary that they must find suitable nutriment in the medium where they live. It even appears necessary that these substances must contain some little nitrogenous matter in order to give the lower organisms the minimum of vitality necessary for the absorption of free nitrogen. But if these nitrogenous principles are too abundant the bacterium subsists by preference at their expense.

**Study of Solutions of Ferric Chloride and Oxalate. Distribution of Ferric Oxide between Hydrochloric Acid and Oxalic Acid.**—George Lemaine.—A thermo-chemical paper, which requires the accompanying diagram.

**Some Derivatives of Licareol.**—Ph. Barbier.—It results from the author's experiments that licareol is a primary alcohol, which may be represented by the formula $C_9H_{15}CH_2OH$. The residue $C_9H_{15}$ admits of two ethylenic connections. Hence licareol is an alcohol with an open chain.

**Constitution of Gallic Blue or Tannin Indigo.**—P. Cazeneuve.—This product is the anilide of gallic acid obtained by the action of nitrosodimethylaniline upon the crystalline product resulting from the action of aniline upon tannin.

**On the Chloramines.**—A. Berg.—Methylchloramine is produced by the action of sodium hypochlorite upon methylamine hydrochlorate. It is a colourless, very volatile liquid of an exceedingly pungent irritating odour. It is rather soluble in water, which dissolves about the tenth of its volume. Dimethylchloramine is obtained in the same manner. It is a liquid almost colourless and of a pungent smell. It boils at 46° under a pressure of 765 m.m. Its density at 0° is 0·986. Water dissolves an eighth of its volume.

**Bornylates of Borneol.**—J. Minguin.—The author examines the influence of bromal upon the camphols. He has experimented upon dextro-borneol $\overset{+}{\alpha}$, levo-borneol $\overset{-}{\alpha}$, borneol $\overset{-}{\beta}$ or levo-isocamphol, borneol $\overset{+}{\beta}$ or dextro-isocamphol, and has given a table of their physical constants.

**Qualitative and Quantitative Analysis of Formaldehyd.**—A. Trillat.—This paper will be inserted in full.

### *Journal fur Praktische Chemie.*
New Series, Vol. xlvi., Parts 20, 21, and 22.

**Action of Gaseous Hydrochloric and Hydrochloric Acids upon Liquid α-Dichlorcyanethyl.** — Dr. J. Troeger.—For this paper we must refer to the original.

**Researches on Alloisomerism.**—Arthur Michael.—These researches comprise three papers: a memoir by A. Michael and G. Tissot on the addition of chlorine to polybasic, non-saturated fatty acids; a comparison of the experimental results with the theorerical deductions from the hypotheses of Le Bel, Van 't Hoff, and Wislicenus; a critique on the hypothesis of Van 't Hoff in its application to the mutual relations of saturated and non-saturated fatty acids. In sulphured wines the sulphurous acid exists in part free and in part as sulphuro-aldehydic acid. Both forms of sulphurous acid can be directly titrated in the manner directed. In wine there are no volatile constituents capable of being oxidised by iodine. The purification of barium sulphate with hydrochloric acid gives occasion to serious errors in the determination of sulphuric acid. The determination is accurate if the barium sulphate is purified with bromine-water and hydrochloric acid. The strictly analytical portions of this paper will be given *in extenso*.

**Knowledge of the Mixed Fatty Aromatic Ketones.**—Ad. Claus.—Not adapted for useful abstraction.

### *Zeitschrift fur Analytische Chemie.*
Vol. xxxi., Part 6.

**Improved Apparatus for Decomposition and Absorption.**—W. Thörner (*Zeit. Angewandte Chemie*).—The decomposition flask, which, according to circumstances, may hold from 200 to 1000 c.c., has a neck 350 m.m. long and 16 m.m. wide, connected by means of a caoutchouc stopper with a suitable light glass jacket and secured to a support. Into this jacket opens an influx and efflux tube for water, so that the neck of the flask forms a reflux-code. The mouth of the flask is closed with a caoutchouc stopper with two perforations. Into one of these fits a small elbow-tube bent at right angles in direct connection with the absorption apparatus. The other end is fitted with a tube funnel with a cock, its lower end reaching almost to the bottom of the flask. Below the cock is a short lateral tube for the introduction of a purified air, carbon dioxide, hydrogen, &c. For determining sulphur in iron, in antimony sulphide, iron sulphide, &c., which are decomposed by means of hydrochloric acid, and the hydrogen sulphide evolved is received in an oxidising absorbent, so that barium sulphate may be ultimately weighed, Thörner connects the decomposition flask with a two globe absorption apparatus. It consists of a glass tube about 12 m.m. wide and 350 to 400 m.m. long, turned slightly upwards and rounded at each end, with a bulb turning upwards. The outer bulb contains 100 and the inner 150 c.c., so that a reflux of the liquid is impossible. The gas has to pass a layer of liquid of about 350 m.m. and to overcome only a slight pressure, a column of water of 30 m.m. The apparatus, besides the purpose above named, can be used for the absorption of ammonia in the examination of water, and in determinations of nitrogen by the Kjeldahl method, the ammonia being driven out by a current of air. The apparatus may also be used for determining $CO_2$ in minerals and in beer, if the necessary protective tubes are introduced. The carbonic acid is absorbed in a potassa apparatus.

**A Syphon for Drawing off Hot Liquids.**—J. Ch. Essner.—From the *Bulletin de la Société Chimique de Paris.*

**Detection of Hyponitric Acid in Sulphuric Acid.**—J. H. Wilson.—From the *Pharm. Journal.*

## MISCELLANEOUS.

**The Royal Society.**—The following is a list of the selected candidates:—Prof. William Burnside, M.A., Prof. Wyndham R. Dunstan, M.A., William Ellis, F.R.A.S., Prof. J. Cossar Ewart, M.D., Prof. William Tennant Gairdner, M.D., Ernest William Hobson, D.Sc., Sir Henry Hoyle Howorth, K.C.I.E., Edwin Tulley Newton, F.G.S., Charles Scott Sherrington, M.D., Edward C. Stirling, M.D., John Isaac Thornycroft, M.Inst.C.E., Prof. James William H. Traill, M.D., Alfred Russel Wallace, LL.D., Prof. Arthur Mason Worthington, M.A., Prof. Sydney Young, D.Sc.

## MEETINGS FOR THE WEEK.

Monday, 15th.—Society of Arts, 8. "Mosaic — its History and Practice," by C. Harrison Townsend. (Cantor Lectures).
Tuesday, 16th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30. (Anniversary).
—— Royal Institution, 3. "Modern Society in China," by Prof. R. K. Douglas.
—— Society of Arts, 8. "Aspects of Federation," by W. B. Perceval.
Wednesday, 17th.—Society of Arts, 8. "Composite Heliochromy," by F. E. Ives.
—— Meteorological, 7.
—— Microscopical, 8.
—— Pharmaceutical, 11 a.m. (Anniversary).
Thursday, 18th.—Royal, 4.30.
—— Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.
—— Society of Arts, 8. "Agrarian Legislation for the Deccan, and its Results," by Sir Raymond West.
—— Chemical, 8. "Observations on the Production of Ozone during Electric Discharge through Oxygen," by W. A. Shenstone and M. Priest. "The Relative Strengths or Avidities of some Weak Acids," by Dr. Shields. "The Boiling-points of Homologous Compounds," Part I., by Dr. James Walker.
Friday, 19th.—Royal Institution, 9. "Poetry and Pessimism," by Alfred Austin.
—— Quekett Club, 8.
Saturday, 20th.—Royal Institution, 3. "Johnson and Wesley," by Henry Craik, LL.D.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1500 tons of MANGANATE OF SODA.

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Manganate of Soda," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

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TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 5000 tons of PROTO-SULPHATE OF IRON.

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Proto-Sulphate of Iron," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.
10th May, 1893,

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TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1700 tons of SULPHURIC ACID.

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Sulphuric Acid," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
10th May, 1893.

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TO LIME MERCHANTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 20,000 tons of LIME, delivery to commence in June next.

Persons tendering will be required to declare in their tenders that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Engineer of the Council, at the County Hall, Spring Gardens, S.W., until Monday, the 5th June, 1893.

Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., and must be endorsed "Tender for Lime," and be sent in not later than 10 o'clock on Tuesday morning, the 6th June, 1893.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE,
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Spring Gardens, S.W.,
10th May, 1893.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1747.

# ON THE ABSORPTION - SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 221).

### *Absorption Spectra produced by the Solution of Chromium Hydroxide in Various Organic Acids.*

It was then thought to be of interest to examine the absorption spectrum given by solution of chromium hydroxide in various other organic acids, for the purpose of seeing how the spectroscopic relations differed from the known differences of constitution of the acids employed. The following acids were chosen for this purpose:—Formic, acetic, propionic, butyric, isobutyric, valerianic, heptylic, monochloracetic, dichloracetic, trichloracetic, tribromacetic, glycollic, lactic, trichlorlactic, malic, tartaric, citric, and isethionic acids.

*Formic Acid* (13).—This acid easily dissolves freshly precipitated chromium hydroxide. The solution has a greenish blue colour by daylight, but in thick layers by lamplight it is red, in thinner layers it is green. The absorption spectrum (13) is made up of two dark bands, 721—714 and 674—666 respectively: also of two fainter and thinner bands lying between them at 704 and 689 respectively. Then the broad absorption which begins with a shadow at 650 becomes dark at 611 and ends at 544, and beyond, continuous absorption from 470.

Several different specimens of chromium hydroxide were used, but the resulting absorption spectra of the various solutions did not differ from the above. In some experiments the solution was digested with an excess of chromium hydroxide; in others an excess of acid was used. Heat also had no effect in altering the position of the bands, but the whole spectrum then became obscured by general absorption.

*Acetic Acid* (13*a*).—This acid also easily dissolves chromium hydroxide. The solution is green by daylight; by lamplight in thick layers it is red, but in thin layers it is green. The solution gave an absorption spectrum which could not be distinguished from that given by the formic acid solution. The absorption spectra given by the two solutions containing formic and acetic acids were superposed by means of a right-angled prism, but no difference in the position of the bands could be observed. Experience showed that minute differences in the positions of narrow bands could best be made evident by making the cross-wires of the telescope coincident with the centre of the band, and fixing the telescope by a clamp to the stand; then, without removing the eye from the eyepiece, placing the solution to be compared in front of the slit, and noting if the centre of the band under examination was coincident with the cross-wires of the telescope. But even by this method no difference could be detected between the two solutions. Thinking that my own spectroscope had not a sufficient dispersion I had placed at my disposal by the kindness of Professor Wiedemann a more powerful instrument. I used in the first instance two prisms, the source of illumination being first the electric light, and secondly sunlight reflected from a heliostat. The dispersion was too great to admit of the bands being distinguished. A very finely ruled grating was now substituted; the source of light being both sunlight and electric light, no change could be detected in the position of the bands in the two solutions under examination.

*Propionic Acid* (14).—This was the next acid used as a solvent for chromium hydroxide. The colour of the solution was the same as in the case of formic or acetic acids. The absorption-spectrum had the same number of bands, which were of the same character as in the cases previously mentioned. On comparison of this absorption-spectrum with that given by the formic acid solution, it was found that the darker bands which could be more easily measured were slightly moved in the direction of the red part of the spectrum. The measurements (14) for the two dark bands are 729—717 and 676—668. The faint band was at 707, while the other faint band, which is more difficult to measure, appears at 689. That is the same as in formic acid, but this is, I believe, accidental for the reason stated above, and it is my impression that the whole spectrum is moved by the same amount nearer the red end of the spectrum.

*Butyric Acid* (15).—This was the next acid used as a solvent for chromium hydroxide. The solution was greenish-blue by daylight, and red or green, according to the thickness of solution examined, by lamplight. It is observable that the more complex acids of this series dissolve less of chromium hydroxide, and with much greater difficulty. The solution obtained gave an absorption-spectrum identical with that given by propionic acid.

*Isobutyric Acid* (15*a*).—This acid does not dissolve chromium hydroxide so readily as butyric acid, but after a time a solution was obtained sufficiently strong. It had a green colour both by daylight and lamplight. The absorption-spectrum of this solution was carefully compared with that given by butyric acid; but it was found that the absorption-spectrum in the case of isobutyric acid was identical with that produced by butyric acid.

*Valerianic Acid* (15*b*).—This acid dissolves chromium hydroxide with great difficulty, but after some time a solution was obtained for examination. The colour of the solution was green both by daylight and lamplight, and gives an absorption-spectrum analogous to the other acids of the series, but the bands are much less distinct than in the case of the acids previously mentioned. I carefully compared this absorption spectrum with that given by formic, acetic, and propionic acids, and I found that there was a slight but distinct movement of all the bands towards the red end of the spectrum, which was more perceptible in the next acid examined.

*Heptylic Acid* (16).—This acid dissolved the chromium hydroxide with difficulty, but after prolonged digestion sufficient was obtained in solution to give an absorption-spectrum with a thickness of 2·5 c.m. The solution was green by daylight and red by lamplight. Its absorption-spectrum was identical—as far as the number of absorption-bands and their relative intensities are concerned—with that given by the other acids of the series; but in the case of the heptylic acid solution the absorption-bands were distinctly moved further to the red end of the spectrum than was the case in any of the other acids previously mentioned.

I confirmed this result by using another spectroscope of greater dispersion, which Dr. Acworth was good enough to lend me, and which he has described.* I avail myself of this opportunity of thanking him for the use of the same.

The measurements made on my own instrument of the heptylic acid solution are as follows (16). The two dark bands are from 732—719 and 681—674 respectively. The two fainter bands are 708 and 695. Then the broad absorption from 650—544, and continuous absorption from 480. The fainter bands at 708 and 695 are not nearly so well marked as the two other darker bands. This remark applies also to all the acids examined belonging to this series; therefore there is considerable difficulty in

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* *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

* J. J. Acworth, "Beziehung Zwischen Absorption und Empfindlichkeit Sensibilisier Platten" (1890).

measuring them, especially in this case, as one requires to work with a slit of small aperture in order to see them at all. In the case of such faint absorption-bands, repeated measurements were made till concordant numbers were obtained.

It has now been shown that when chromium hydroxide is dissolved in the fatty acids previously mentioned, absorption-spectra are produced which are quite analogous in structure; and we have here another instance of the movement of the absorption-bands towards the less refrangible end of the spectrum as the molecular complexity of the body examined increases. But the known difference of the structure of the isobutyric acid molecule from that of the butyric acid molecule does not appear to alter the position of the absorption-bands.

It is further observable that the higher acids of the fatty acid series give—when chromium hydroxide is dissolved in them—bands less distinct and less dark than is given by the lower acids of the same series. The broad absorption in the green part of the spectrum of these chromium compounds is usually so indefinite at the edges that it is impossible to say if it also moves with the other bands, but there is reason to believe that it does.

It is remarkable that an acid so different in constitution, and in almost every other respect to the fatty acids as succinic acid is, should, when chromium hydroxide is dissolved in it, give an absorption-spectrum practically identical with that given by propionic or butyric acids when similarly treated. Yet it is so, for I repeated the experiment with three different specimens of chromium hydroxide without any different result; nor was I able to observe that any decomposition of the acid occurred. At present I am not able to give any explanation of this remarkable spectroscopic analogy.

To be continued).

# A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

## First Paper: The Analysis of Baric Bromide.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 223.)

### *Balance and Weights.*

The balance and weights were identical with those used in the latter part of the investigation upon copper (*Proc. Amer. Acad. Arts and Sciences*, xxvi., p. 242), hence a further description of them is unnecessary. The weights were gently and carefully rubbed, and again standardised with reference to each other; a proceeding which yielded values essentially identical with the two previous standardisations. The first ten-gramme weight was also compared from time to time with the platinum weight which had been carefully standardised in Washington (*loc. cit.*) in order to test its constancy.

| | | True Grammes. |
|---|---|---|
| Oct. 18, 1891 | Ten-gramme weight | = 10·00023 |
| May 16, 1892 | ,, ,, | = 10·00023 |
| Nov. 1, 1892 | ,, ,, | = 10·00022 |
| Nov. 2, 1892 | ,, ,, | = 10·00020 |

The second ten-gramme weight, which was much less used, remained quite constant in value.

Throughout the present investigation the method of weighing by tares was universally adopted. A vessel to be weighed was placed upon the left hand scale pan, balanced with common gilded weights, and then replaced by a similar vessel which weighed a few milligrms. less. The exact amount of this extra tare having been determined with the rider, the counterpoise was replaced by the original vessel and the rider removed, in order to determine if the centre point had changed. When only a slight change had taken place, the reading for the counterpoise was compared with the mean of the two readings for the original vessel. In the rare cases when the change exceeded the equivalent of the thirtieth of a milligrm., the vessels were alternately substituted for each other until constancy was reached. A substance to be weighed was of course placed in such a tared vessel, and after substitution the deficiency of the counterpoise was made up with standard weights. The difference between the tares on the left hand scale pan indicated the observed weight in air of the substance taken. It was found convenient to tabulate the results in the form given in Table below.

The lowest right hand figure represents the true weight of the substance taken, if the Sartorius ten-gramme weight is taken as the standard. Reduced to the Washington standard the value becomes 1·80934; but this last correction is in no case applied in the work which follows.

The method used in the case of hygroscopic substances, and most other precautions, are given at length in the paper already quoted. In weighing a crystallised salt it was usually necessary to weigh the crucible while filled with ordinary moist air, hence the counterpoise crucible was exposed to the same conditions.

During the latter part of the investigation the balance was kept in a small room built entirely inside of the main laboratory. The absence of outside windows in the small room caused a notable absence of air currents and rapid changes of temperature, while its glass walls supplied plenty of light.

It is almost needless to state that, while the weights of the apparatus were not reduced to the vacuum standard,—on account of the method of weighing, which rendered such reduction unnecessary,—the weight of every substance used was corrected in the manner shown above for the difference between the weight of air displaced by it and that displaced by the corresponding brass weights. Where the specific gravity of the substance was not already accurately known, it was carefully determined for this purpose.

### *The Spectroscopic Detection of Calcium and Strontium in the Presence of Barium.*

In the course of the search for a typical barium salt it became important to determine how small an amount of calcium and strontium could be detected in the presence of large amounts of barium. The most sensitive method is naturally the spectroscopic one, but no literature giving the degree of sensibility seemed to be at hand.

The first phase of the problem to be investigated was the determination of the amount of calcium and strontium which could be detected in the absence of barium. Hence a standard solution of calcium and strontium was prepared containing 0·8 m.grm. of each metal to the c.c. This solution was successively diluted and tested by means of a well made single prism spectroscope with an

| | Common Weights: Rt. hand pan. | Tare: Standard Wts. L. hand pan. | Cor. to Standard Weights. | Corrected Standard Weights. | Correction to Vacuum. | True Wt. of Substance taken. |
|---|---|---|---|---|---|---|
| | Grms. | Grms. | M.grms. | Grms. | M.grms. | Grms. |
| Weight of crucible + substance .. .. | 22·0890 | 1·80986 | −0·05 | 1·80981 | | |
| Weight of crucible alone .. .. .. | 20·2797 | 0·00081 | 0·00 | 0·00081 | | |
| Wt. of substance, cryst. baric bromide | 1·8093 | 1·80905 | | 1·80900 | +0·30 | 1·80930 |

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* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

adjustable slit. A drop of the solution was supported upon a coil of wire containing 0·018 c.c., similar to that suggested by Truchot (*Comp. Rend.*, lxxviii., 1022) and so ably used by Gooch and Hart (*American Journal of Science*, [3], xlii., 448); the writer is much indebted to this paper for valuable hints. No attempt at quantitative analysis was made, the present problem being merely the determination of the limit of visibility.

*Results.*

| Dilution. | | | Weight of Ca and Sr vapourised. | Observations. |
|---|---|---|---|---|
| Solution | : | Water. | M.grms. | |
| 1 | : | 0 | 0·014 | Brilliant. |
| 1 | : | 5 | 0·003 | ,, |
| 1 | : | 10 | 0·0014 | Very plainly visible. |
| 1 | : | 20 | 0·0007 | ,, ,, ,, |
| 1 | : | 40 | 0·0004 | Plainly visible. |
| 1 | : | 100 | 0·00014 | Both visible. |
| 1 | : | 200 | 0·00007 | Both scarcely visible. |
| 1 | : | 400 | 0·00004 | Both invisible. |

Hence seven hundred-thousandths of a m.grm. is about the limit of visibility under these conditions. It is remarkable that this result should be essentially identical with Bunsen's result obtained by a different method (compare Vogel's "Spectralanalyse irdischer Stoffe," 1877, pp. 92, 94).

It has long been known (compare Vogel's "Spectralanalyse irdischer Stoffe," 1877, p. 99) that the best method for detecting small quantities of strontium and calcium in the presence of barium is to evaporate the the solution of the chlorides to small bulk, precipitate most of the baric chloride by means of alcohol, and test the filtrate. From this filtrate, by means of two or three repetitions of the fractionation with alcohol, it is possible to eliminate nearly all the barium. It is evident, on the other hand, that if the precipitate is dissolved and re-precipitated several times, all the calcium and strontium must go into the mother liquors. This is one of the most rapid methods of obtaining pure baric chloride; it served for the preparation of the material used in the succeeding experiments.

In the first experiment half a m.grm. of calcium was added to the solution of three grms. of very pure baric chloride. Upon the usual fractional treatment a most brilliant calcium spectrum was obtained from the mother liquor. One-fifth of a m.grm. of calcium in another experiment gave similar results. For a third experiment one-fiftieth of a m.grm. each of calcium and strontium was added to five grms. of crystallised baric chloride. The mother liquor from the first precipitation by alcohol was evaporated to dryness and extracted with alcohol. Calcium was very evident in the extract, but no trace of strontium. The reason for the apparent absence of the latter metal is to be found in the fact that the mother liquor was evaporated to dryness. To prove this, the same amount of materials were fractionally precipitated three times, and a very evident strontium spectrum was given by the last mother liquor. In the fifth trial, only one two-hundredth of a m.grm. of strontium was used. Upon three fractionations no strontium could be detected, but upon dissolving and re-precipitating each of the precipitates once more a faint test for the metal was found in the final mother liquor. This is evidently about the limit so far as strontium is concerned. Calcium may be detected when it is present in quantities much less than the two-hundredth of a m.grm., because of the ready solubility of its chloride in alcohol. The baric chloride used gave no trace of the calcium or strontium lines after most careful fractionation.*

From these experiments it may be concluded that when a baric salt shows no trace of the allied metals upon the treatment just described, it does not contain a weighable amount of them. Nevertheless, in the work which follows, the purification was usually continued long after the visible traces of strontium and calcium had been eliminated.

(To be continued).

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* A trace of sodium was always found in even the purest specimens. It is probable that this trace was derived from the air during the course of fractional treatment necessary to eliminate the barinm.

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# INSTRUCTIONS FOR THE EXAMINATION AND JUDICIAL DECISION ON PORTIONS OF ANIMAL ORGANISMS INTENDED FOR HUMAN FOODS.*

By WILHELM EBER.

(Concluded from p. 222).

If fumes were present the gaseous column becomes clear in five to ten minutes, and the glass after careful shaking is ready for another test. Such a glass may serve for many hundred trials without requiring a renewal of the liquid. A renewal is necessary as soon as the inner sides of the glass have become dirtied, or parts of the specimen have fallen into the liquid, or the reagent is spoiled. The last is the case as soon as a drop of pure water placed on the glass produces a mist, or ammonia no longer forms a cloud.

(*e*) The reaction is ascertained by pressing a narrow slip of moistened litmus paper upon the specimen by means of a clean knife (not the fingers, which have often an acid reaction). After ten minutes the papers are lifted off the object, laid upon white paper, and compared with another slip of the original litmus paper, also moistened.

### 3. *Condition Internally.*

(*a*) The surface is washed clean from any adhering deposit.

(*b*) A deep section is made extending at least to the middle of the object, or the interior is laid bare in some other manner.

(*c*) Colour and general appearance of the recent sections (escape of gas-bubbles ?).

(*d*) The odour is ascertained on an unobjectionable portion of the specimen which has not come in contact with any other portion.

(*e*) The reaction is determined with litmus paper.

(*f*) Ammonia test for putridity.

(*g*) Consistence.

(*h*) Change of freshly-cut surfaces on exposure to air.

(*i*) Boiling test. It is, in general, applied only to salted or pickled meat in order to ascertain if such meat is thoroughly pickled (permanence of red colour after boiling, firm consistence), and whether odours not perceptible in the cold are evolved on heating.

(*j*) Test for hydrogen sulphide.

The diagnosis may indicate:—

1. Simple acidity. Faintly acid or amphoteric reaction, specific odour of the animal species, no ammoniacal fumes.

2. Acid fermentation. Strongly acid reaction, no ammoniacal fumes.

3. Putridity. Reaction alkaline, amphoteric, or neutral. (Traces of grey mist which disappear in passing from the glass rod to the level of the liquid are unmeaning). The specimen is putrid if the decomposition indicated by the ammonia test has reached such a height that the portions affected cannot be separated from the remainder.

4. Mixed processes. Reaction acid, ammoniacal fumes. In practice such processes are pronounced incipient putrefaction.

5. Decompositions of indefinite character. No action upon litmus paper; merely changes of colour, (*e.g.*, luminosity in the dark) in odour and consistence. Includes foods of inferior value.

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* From the *Zeit. Anal. Chemie.*

### ON A
## NEW METHOD FOR THE BACTERIOLOGICAL EXAMINATION OF WATER.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S., &c.

### *Introduction.*

THE study of microbes is not only of the greatest value to the pathologist and physician, but concerns the chemist, sanitarian, brewer, manufacturer, and agriculturist; in fact, it concerns all, for there is not a moment of our lives in which we are not in contact with "the unseen mist of organic forms." It may be said that microbes are omnipresent,—that they are always present in water, air, and soil. Their numbers vary, however, with the nature of the water, air, and soil; the time of the year and various climatic conditions also influence their rate of increase.

Although in the present paper we deal with the microbian examination of *water*, it may be stated that many microbes present in water are also found in the air and soil. The state of the atmosphere influences to a certain extent the number of microbes present in water. For instance, after a considerable amount of rain the atmosphere contains fewer microbes than it does in fine weather; but, on the other hand, rivers and natural waters generally contain (as a rule) larger numbers of microbes in wet than in fine weather. Then, again, water percolating through soil or strata rich in microbes (such as surface waters), or water polluted with sewage, contains larger numbers of microbes than that derived from deep-seated springs, or from a non-polluted source.

In addition to the above mentioned conditions the number of microbes in any water depends upon the amount of organic matter present. A water rich in organic matter always contains a larger number of microbes (in a given volume) than a water almost free from such matter; but if the organic matter is rapidly converted by oxidation into the ultimate products of decomposition, the ordinary microbes of putrefaction are no longer able to obtain the necessary material for subsistence; nevertheless, the true water microbes, according to Meade Bolton (*Zeit. fur Hygiene*, Bd. i., p. 76) and others, can still flourish and even multiply in distilled water. But, as Prof. P. F. Frankland (*Journ. Soc. Chem. Ind.*, 1887, vol. vi.) justly remarks, "it should be observed that when it is stated that an organism has multiplied in distilled water, it must be understood that this multiplication has doubtless taken place at the expense of those *traces* of organic matter which must of necessity be present in experiments of this kind."

As the bacteriological examination of water has now come to be a subject of great importance, I venture to describe a new bacteriological method for examining any sample of water; but before doing so it will be interesting to allude to the methods in use for the same purpose.

### *Methods for Examining Waters for Microbes.*

The principal methods used for the *qualitative* examination of water for microbes are those of Prof. J. Burdon Sanderson (Reports of the Medical Officer of the Privy Council, 1870) and the late Dr. R. Angus Smith (*The Sanitary Record*, 1883, p. 344), while the methods used for the *quantitative* examination of water for microbes are (1) the plate-cultivation process, introduced by Dr. R. Koch (*Mittheilungen aus dem Kaiserlichen Gesundheitsamte*, Bd. 1) in 1881, and (2) the process of fractional cultivation in bouillon or other liquid media, which is largely used by M. Miquel[*] and other French authorities.

1. *The Plate-Cultivation Method.*—This method consists in taking a known small quantity (say 1 c.c.) of the water and mixing it with melted nutrient gelatin (sterile) contained in a stock-tube.[*] After shaking the mixture it is rapidly poured out upon a sterilised glass plate, then allowed to solidify, and finally placed in a damp chamber kept at about 22° C. After a few days' incubation, colonies make their appearance on and in the layer of gelatin. The gelatin plates are inspected every twenty-four hours, until the day when one or more of the colonies overlap one another, or until liquefaction of the gelatin destroys the solid *substratum*, and with it the collective seed-bed of microbes. The colonies so produced are counted by means of the eye or lens with the aid of Wolffhügel's apparatus.

2. *The Fractional-Cultivation Method.*—This method consists of two operations: (*a*) the dilution process, (*b*) the distribution of bouillon of the water diluted. To dilute the water the authorities of the Laboratoire de l'Observatoire de Montsouris (where this method is largely used), employ flasks varying in capacity from 30 to 2000 c.c. These flasks are covered with caps containing sterilised cotton-wool plugs. Each flask is half filled with a known volume of distilled water, which is then sterilised in a digester for more than an hour at 110° C. After agitation of the water under investigation, it is diluted with from 15 to 1000 c.c. of sterilised water (*i.e.*, according to its richness in microbes), and then 1 c.c. of the diluted sample is taken up by means of a sterilised capillary pipette. This quantity of water is distributed among 36 small flasks (each 15 c.c. capacity) containing sterilised beef bouillon. After the sterilised cotton-wool plugs have been replaced, all the flasks are placed in an incubator at 30—35° C. during a period of at least fifteen days, when the microbian colonies are counted.

It is stated that by this method there is no overlapping of the colonies, and a much higher temperature (during the incubation) can be used with liquid than with solid media. There is, however, a great drawback in using the fractional method, viz., that the colonies undergo movements of translation; and consequently there are no means of preventing the overlapping which has been alluded to. Moreover, the ptomaines, &c., formed during the growth of some microbes[†] are dissolved, more or less, in liquid media, but not so when solid media are used, and in liquid media these products of microbian activity interfere with the growth of some microbes. This is a phenomenon which I have frequently observed.

Concerning the disadvantage of the low temperature at which Koch's nutrient gelatin melts (20° C.), it may be stated that Professor P. F. Frankland (*Journ. Soc. Chem. Ind.*, 1885, vol. iv.) has found that by using 150 grms. of gelatin instead of 100 grms.,[‡] the melting-point of the nutrient gelatin is considerably raised. This was an important modification in the composition of Koch's solid medium, which I have taken advantage of in my own investigations.

There is no doubt, taking into consideration the *pros* and *cons*, that Koch's method is superior to that of fractional cultivation in bouillon. Even M. Miquel ("Annuaire de l'Observatoire de Montsouris," 1889, p. 401), who uses the latter method, says: "Cette méthode (de M. Koch) est simple et très élégante; elle rend surtout de réels services quand il importe de séparer les microbes les uns d'avec les autres; elle permet le triage rapide des organismes contenus dans les eaux."

### *A New Method for the Examination of Water.*

The following method, which I am desirous of bringing before the notice of chemists, bacteriologists, and others, is based on that of Dr. W. Hesse for the examination of

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[*] "Annuaire de l'Observatoire de Montsouris," 1877-91; and his "Manuel Pratique d'Analyse Bactériologique des Eaux," 1891.

[*] If the original sample of water is very impure (*i.e.*, rich in microbes), it should be first diluted with sterilised distilled water.

[†] I have shown that some microbes of putrefaction are capable of giving rise to ptomaines in artificial media. (See *Comptes Rendus*, vol. cx., p. 416; *Bull. Soc. Chim. Paris*, Series 3, t. 7, p. 332; *Centralblatt fur Bakteriologie*, Bd. vii., p. 808; and the references to my work in Gautier's "Cours de Chimie," t. 3, p. 268).

[‡] The original quantity per litre, as used by Koch.

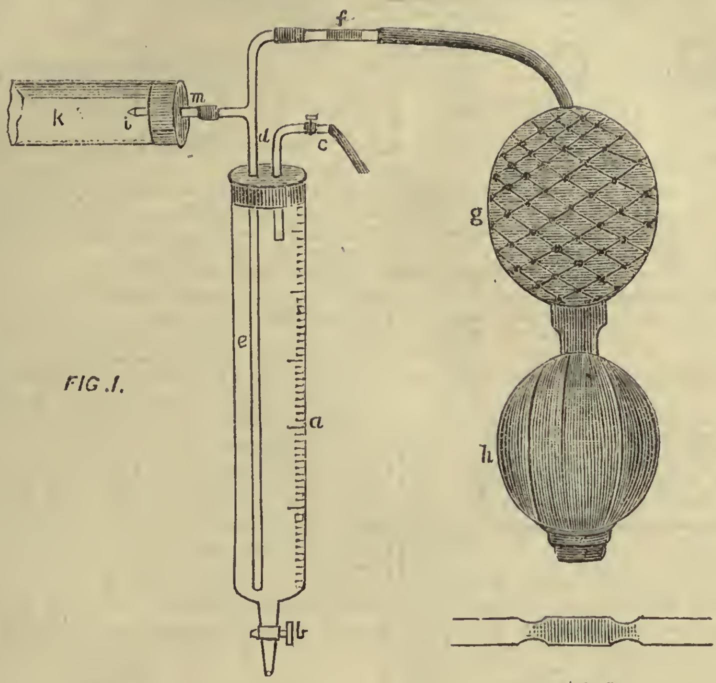

FIG. 1.

FIG. 2.

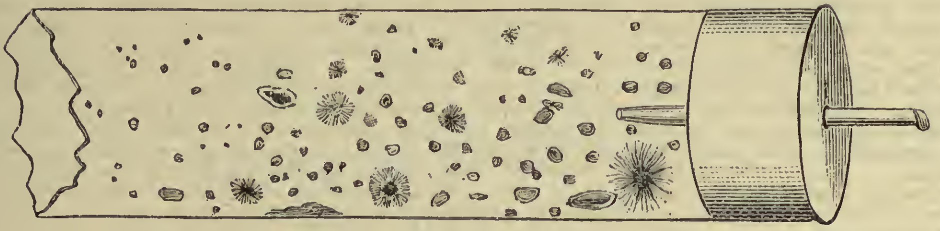

FIG. 3.

air (*Mittheilungen aus dem Kaiserlichen Gesundheitsamte*, Bd. 2).

The apparatus used in this new method is illustrated in Figs. 1 and 2. After having collected the sample of water with all the precautions mentioned by Frankland (*Journ. Soc. Chem. Ind.*, 1885, vol. iv.), 1 c.c. is introduced into the sterilised pipette *a* by suction at *c*; and, if necessary, this sample is diluted with a small quantity of sterilised distilled water by taking off the indiarubber tube *c*, and sending a stream of sterilised water through the tube *d* into the graduated pipette *a*. The taps *b* and *c* being closed, a current of sterilised air is passed to the bottom of the water by means of an ordinary hand spray-producer (*g*, *h*). This causes the sample of water to pass up the tube *e*, and finally to issue as a fine spray through the nozzle *i*. This spray is distributed over the surface of a glass tube (90 c.m. × 5 c.m.) which has previously been coated internally with a thin layer of nutrient gelatin.

After the whole of the water has been sprayed into the tube, which is practically an easy operation, the small glass tube *m* is hermetically sealed, and the long cultivation-tube *k* is placed in an incubator, or a warm place for colonies to develop (Fig. 3 shows the colonies). The liquid particles introduced into the cultivation-tube *k* subside immediately, although they may be carried to three quarters of the length of the tube, the opposite end of which is plugged with sterilised cotton-wool.

The whole of the glass portion of the apparatus is readily sterilised by means of a hot-air steriliser, and previously washing in a solution of mercuric chloride (1 : 1000), alcohol, and sterilised water.* The indiarubber portion of the apparatus is sterilised by immersing it in a solution of mercuric chloride, and finally in sterilised water. It may be stated that the air from *g h* passes through a tight-fitting plug of sterilised cotton-wool, *f* (see also Fig. 2); in other words, it is filtered by this means, and the influx of air (through the apparatus) is also filtered through the cotton-wool plug at the opposite end of the cultivation-tube (not shown in the figures). In using this apparatus the strictest attention was paid to the sterilisation of it in every detail.

By this method I have obtained the following average results, which are compared with those obtained by using Koch's method. In each case the same sample of water was used. (See Table, next page).

The two series of experiments were conducted under similar conditions,—that is, as far as length of time of incubation, temperature, composition of the nutrient gelatin, &c. Concerning this method it may be remarked:—

(1) There is no burying, so to speak, of the microbes in the medium when the latter is melted, as is the case

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* In the case of the cultivation-tube *k* before the introduction of the nutrient gelatin.

| Samples of water collected from— | Colonies from 1 c.c. water by new method. | Colonies from 1 c.c. water by Koch's method. |
|---|---|---|
| River Thames at Richmond.. .. | 6900 | 6200 |
| Serpentine in Hyde Park, London | 21300 | 21160 |
| River Irwell, Manchester .. .. | 8200 | 8100 |
| River Medlock, Manchester .. .. | 15320 | 15260 |
| River Seine, Paris (taken near Institut de France) .. .. .. | 18400 | 17980 |
| River Seine, Paris (taken in vicinity of St. Cloud) .. .. .. .. | 20300 | 20125 |
| River Seine, Rouen.. .. .. .. | 27200 | 26700 |
| Lake in the Parc des Buttes Chaumont, Paris .. .. .. | 32100 | 31900 |
| Lake in the Parc de Montsouris, Paris .. .. .. .. .. .. .. | 34360 | 33920 |
| River Witham, Lincoln.. .. .. | 11525 | 11050 |
| Rain-water . .. .. .. .. .. .. | 644 | 620 |
| Pond water (stagnant), Lincoln .. | 40960 | 40240 |
| River Lea, Birmingham . .. .. | 14980 | 14560 |

with Koch's method, the small particles of water being deposited on the solid medium. It appears that some aërobic microbes perish when immersed beneath the surface of the melted gelatin (Koch's method).

(2) The microbes deposited on the solid medium grow and multiply on the spot where they were *first* planted. There is not the smallest movement of translation; consequently this is a great advantage over the method of fractional cultivation in a *liquid* medium, and it is more accurate than Koch's method, in which the water is introduced by means of a pipette into the melted gelatin, whereby many microbes may become crowded together as the gelatin solidifies.

(3) The tube remains practically closed against any accidental contamination with microbes of the air. This is a great advantage over Koch's method, for in the latter method such contamination is possible during the preparation of the plate cultivation.

(4) The sample of water (of known volume) is introduced directly into the sterilised apparatus.

(5) By gently blowing air into the graduated tube (after spraying), every particle of moisture is sent into the tube *k*.

(6) The new method may appear to be favourable for the growth of aërobic microbes, and unfavourable for the growth of anaërobic microbes. But this is not so; for all the common forms peculiar to different kinds of water* readily make their appearance when this method is used.

In conclusion, it may be stated that this method has all the advantages of that of Koch, in addition to several others which have already been mentioned.

*Explanation of the Plate.*

FIG. 1 shows the general arrangement of the apparatus when ready for spraying the sample of water into the cultivation-tube. The indiarubber balloon (*h*) is compressed with the hand, and *g* is an air-receiver.

FIG. 2 is an enlargement of *f* in Fig. 1, and shows the way of fixing the cotton-wool plug for filtering the air.

FIG. 3 shows one end of the cultivation-tube with colonies after several days' incubation.

**The Chicago Exhibition.**—We are requested to state that the New York Section of the American Chemical Society has appointed a Committee, of which Dr. H. Carrington Bolton is Chairman, to receive distinguished chemists who may pass through New York on their way to or from Chicago. Chemists arriving in New York are requested to send their names and addresses to Professor Morriss Loeb, University of the City of New York, who is Secretary of the Committee.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, April 20th, 1893.*

Dr. ARMSTRONG, President, in the Chair.

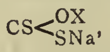
(Concluded from p. 226).

*2. "*The Interaction of Alkali Cellulose and Carbon Disulphide: Cellulose Thiocarbonates.*" By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

*Alkali cellulose* has been further investigated by the authors, both in the form known as "mercerised" cellulose (cotton) and in the form of gelatinous hydrates which dissolve in alkaline solutions. The corresponding benzoates which have been prepared afford evidence as to the number of active OH groups; the maximum appears to be four, cellulose being expressed as $C_{12}H_{20}O_{10}$.

*Cellulose thiocarbonates* result from the interaction of alkali cellulose and carbon disulphide in the molecular proportions $C_{12}H_{20}O_{10} : 4NaOH : 2CS_2 : 30—40H_2O$. The product swells up enormously on treatment with water, and finally completely dissolves, but undergoes change, hydrated cellulose and products of interaction of the alkaline hydrate and carbon disulphide being formed.

From the study of the composition of a large number of these products, the authors are led to assign to the series of compounds the general formula—



$$CS{<}^{OX}_{SNa},$$

X representing the cellulose "residue" or rather an alkali cellulose residue or radicle of variable dimensions.

These thiocarbonates of cellulose yield solutions of extraordinary viscosity, and from the property they possess of undergoing change, regenerating cellulose, promise extended applications. The further investigation of the compounds is in progress.

In conclusion, the bearings of the results and other recent contributions to cellulose chemistry are discussed with reference to the molecular constitution of the typical members of the series.

3. "*Sulphocamphylic Acid.*" By W. H. PERKIN, jun.

In the course of a series of researches on camphoric acid and its derivatives, the author has for some time been engaged in submitting to detailed examination the sulphocamphylic acid which Walter (*Jahresb.*, xxi., 272; xxiv., 392) first prepared by heating camphoric acid with sulphuric acid. In the formation of this acid, quantities of carbonic oxide are evolved, the decomposition being apparently represented by the equation—

$$C_{10}H_{16}O_4 + H_2SO_4 = C_9H_{16}SO_6 + H_2O + CO.$$

After carefully verifying the formula of sulphocamphylic acid by the analysis of the acid and of some of its salts, the author next studied the behaviour of the acid on distillation. When small quantities of the acid are rapidly heated in small retorts, vigorous decomposition takes place, a small quantity of a colourless oily substance, which soon solidifies, passing over, a large amount of carbonaceous matter being left in the retort.

After re-crystallisation from formic acid, the solid product melts at 134—135°; on analysis it gives numbers agreeing with the formula $C_9H_{14}O_2$, and is a monobasic acid, its formation from sulphocamphylic acid being apparently represented by the equation—

$$C_9H_{16}SO_6 = C_9H_{14}O_2 + H_2SO_4;$$

it yields a silver salt of the formula $C_9H_{13}AgO_2$. The acid distils with only slight decomposition, and volatilises with steam; it dissolves in cold sulphuric acid without decomposing, but on warming the solution at 90° a sulphonic acid is readily formed: this appears to be re-

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* See the author's "Manual of Bacteriology," p. 287 (W. Heinemann).

generated sulphocamphylic acid, but no analysis of the product has as yet been carried out.

A neutral solution of the sodium salt of sulphocamphylic acid is readily oxidised by potassium permanganate at 0°, forming a variety of products: from these the author has succeeded in isolating small quantities of a beautifully crystalline compound, melting at 254°, which on analysis was found to possess the remarkable formula $C_{18}H_{22}O_7$. This substance is a dibasic acid, the silver salt having the formula $C_{18}H_{20}O_7Ag_2$; when heated at 140° the acid loses 1 mol. prop. of water, and is converted into a compound of the formula $C_{18}H_{20}O_6$.

The *dimethylic salt*, prepared by treating the compound of the formula $C_{18}H_{22}O_7$ with methyl alcohol and sulphuric acid has the formula $C_{20}H_{24}O_6$, instead of $C_{20}H_{26}O_7$ as might have been expected.

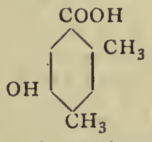
The compound of the formula $C_{18}H_{22}O_7$ affords a *dihydroxime*, $C_{18}H_{22}N_2O_6$, which crystallises from ether in scales which do not melt at 250°. Excess of acetic anhydride converts this hydroxime into a *monoacetate*, $C_{18}H_{21}N_2O_6(C_2H_3O_2)$, m. p. 195°. By the action of phenylhydrazine it is converted into a dihydrazone, $C_{30}H_{34}N_4O_5$; this compound crystallises from acetic acid in brilliant red prisms which decompose at 232°.

The acid of the formula $C_{18}H_{22}O_7$ is readily reduced by sodium amalgam, combining with 2 atoms of hydrogen and losing 1 mol. of water, the product having the composition $C_{18}H_{24}O_6$. This reduction product is a dibasic acid, which does not melt at 300°; the *silver salt*, $C_{18}H_{22}Ag_2O_6$, was analysed.

Among the many remarkable decompositions of the substance of the formula $C_{18}H_{22}O_7$, the investigation of which is not concluded, the behaviour of this acid towards sulphuric acid is perhaps the most interesting. The acid readily dissolves in concentrated sulphuric acid; if the solution be warmed at 90—95° decomposition rapidly takes place, and on pouring the product into water a yellow flocculent substance separates, which is a new monobasic acid of the formula $C_9H_{10}O_3$; the formation of this acid may be represented by the equation—

$$C_{18}H_{22}O_7 = 2C_9H_{10}O_3 + H_2O.$$

A careful investigation of this compound has proved that it is a *hydroxymetaxylenecarboxylic acid* of the constitution represented by the formula—



In the course of the prolonged investigation of this acid which was necessary before its constitution could be determined, the following derivatives were prepared and analysed:—

*Silver salt*, $C_9H_9O_3Ag$; *dimethylic salt*,—

$$C_9H_8O_2(OCH_3)\cdot CH_3$$

(oil); *methylic salt*, $C_9H_8O_2(OH)\cdot CH_3$ (m. p. 149°); *isomethylic salt*, $C_9H_8O_2(OCH_3)H$ (m. p. 171°); *diethylic salt*, $C_9H_8O_2(OC_2H_5)\cdot C_2H_5$ (m. p. 51°); *ethylic salt*, $C_9H_8O_2(OH)\cdot C_2H_5$ (m. p. 135°); *isoethylic salt*, $C_9H_8O_2(OC_2H_5)H$ (m. p. 174°).

A *dinitro-acid* of the formula $C_9H_8(NO_2)_2O_3$, formed by the action of nitric acid; this crystallises in yellow needles which melt at 203—205°; it behaves as a dibasic acid, giving a silver salt of the formula—

$$C_9H_6Ag_2(NO_2)_2O_3.$$

When exposed to the action of bromine vapour, it is converted into a *dibromo-derivative*, $C_9H_8Br_2O_3$, which crystallises in colourless prisms and melts at 205°.

The isomethylic salt is readily oxidised by an alkaline solution of potassium permanganate, yielding a substance of the formula $C_7H_5(OCH_3)(COOH)_2$, which crystallises in colourless needles melting at 250°. When heated with a fuming solution of hydrogen iodide, this dibasic acid is readily decomposed, yielding the corresponding phenolic compound, $C_7H_5(OH)\cdot(COOH)_2$, which on investigation has proved to be identical with the *hydroxymethylterephthalic acid* of the formula—

$$OH : CO_2H : Me : CO_2H = 1 : 2 : 4 : 5,$$

prepared by Jacobsen (*Ber.*, xvi., 191). This result proves that the acid of the formula $C_9H_{10}O_3$ has the constitution assigned to it above, *i.e.*, that of hydroxymetaxylenecarboxylic acid ($COOH : CH_3 : CH_3 : OH = 1 : 2 : 4 : 5$).

The author hopes in a short time to be able to publish the details of these and many other experiments not mentioned in this abstract, and to be in a position to explain the relationship between the compounds represented by the formulæ $C_{18}H_{22}O_7$ and $C_9H_{10}O_3$; as also to suggest a constitutional formula for sulphocamphylic acid.

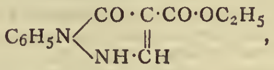
4. "*Magnesium Diphenyl.*" By Lothar Meyer.

W. R. Hodgkinson, in a recent note (*Proc. Chem. Soc.*, 1893, p. 80), refers to a substance not yet obtained pure which he suggests may be magnesium phenyl; this induces me to state that magnesium diphenyl was prepared in my laboratory last year by Hermann Fleck, and described by him in his inaugural dissertation ("Ueber Magnesium Alkyle"; Tübingen, 1892), and that an account of his work will be published in Liebig's *Annalen*.

*Magnesium diphenyl*, $MgEt_2$, is obtained by the interaction of magnesium and mercury diphenyl at 200—210° in the form of a very voluminous powder, insoluble in all ordinary liquids, but soluble in a mixture of ether and benzene. It is spontaneously inflammable; on slow oxidation it yields a phenate; water converts it into benzene and magnesium hydrate; it affords bromobenzene and magnesium bromide on treatment with bromine, triphenylmethane on treatment with benzal chloride, and diphenylphosphine chloride and more complex compounds when subjected to the action of phosphorous chloride. It has the advantage over mercury diphenyl that it readily exchanges both phenyls for other radicles, and does not yield a compound corresponding to mercury phenyl chloride. The study of the magnesium alkyls is being continued in the Tübingen Laboratory.

5. "*The Formation of Pyridine Derivatives from Unsaturated Acids.*" By S. Ruhemann, Ph.D.

An account is given of the continuation of previous work by the author on the same subject. It is now shown that *ethylic methyldicarboxyglutaconate* is converted by aqueous ammonia into *methylmalonamide* and *ethylic amidoethylenedicarboxylate*, and that phenylhydrazine acts on it, forming *ethylic methylmalonate* and the ammonium compound of the *pyrazolon*,—



$$C_6H_5N\begin{cases} CO\cdot C\cdot CO\cdot OC_2H_5 \\ \qquad\ \| \\ NH\cdot CH \end{cases},$$

which has been previously described.

*Ethylic methylglutaconate* is converted by the action of aqueous ammonia into *β-methyl-αα'-dihydroxypyridine*; on reduction with zinc dust, the compound furnishes β-picoline; on oxidation with ferric chloride, it affords a yellow colouring matter.

*Ethylic ethyldicarboxylglutaconate* is converted by aqueous ammonia into *ethylmalonamide* and *ethylic amidoethylenedicarboxylate*; and by phenylhydrazine into a *pyrazolon* and *ethylic ethylmalonate*.

When heated with aqueous ammonia in a closed tube at 100°, *ethylic ethylglutaconate* is converted into *ethylic dihydroxypyridine*, which yields a yellow colouring matter, probably a hydroxyquinone, on oxidation with ferric chloride.

6. "*Chlorinated Phenylhydrazines.*" Part II. By J. T. Hewitt, Ph.D.

The author, in continuation of his previous work, describes the *sulphate* and *oxalate* of *orthochlorophenyl-*

*hydrazine.* Unlike the meta- and para-derivatives, this hydrazine does not form a urazole when heated with biuret. The ethylic salt of the hydrazone of pyruvic acid occurs in yellow needles melting at 68°, not at 168° as previously stated; it is insoluble in alkalis.

*Metachlorophenylhydrazine*, which has been prepared and described by Willgeiodt and Mühe, forms a crystalline *hydrochloride*, *sulphate*, and *nitrate*. A solution of the hydrochloride and potassium cyanate interact to form a *semicarbazide* melting at 155°; the corresponding *thiosemicarbazide* is obtained when phenyl mustard oil is used. The hydrazine furnishes a *urazole* when heated with biuret.

The metachlorophenylhydrazone of benzaldehyd crystallises in colourless needles melting at 133—134°; the corresponding hydrazone of pyruvic acid is crystalline, and melts at 163°.

*Parachlorophenylhydrazine* is also shown to form a similar *semicarbazide* and *hydrazones* of benzaldehyd and pyruvic acid.

7. "*The Oxidation of Tartaric Acid in Presence of Iron.*" By H. J. H. Fenton, M.A.

If a small quantity of hydrogen peroxide be added to a solution of tartaric acid containing a trace of ferrous salt, a yellow colour is produced which changes to violet on adding alkali; an excess of the peroxide must be avoided. As other organic acids do not behave in this manner, the interaction may be utilised in detecting tartaric acid. The violet colour is discharged by acids, sulphuric acid producing a transient green colouration, and is reproduced by alkali.

The compound which gives the colour with ferric salts is crystalline, and appears to be represented by the formula $C_2H_2O_3$. It is best obtained by dissolving tartaric acid in a limited quantity of boiling water, and then adding about $\frac{1}{20}$th of its weight of reduced iron; the liquid is then heated until clear. After the solution has been well cooled, hydrogen peroxide is carefully added drop by drop, the temperature being maintained constant until the liquid is nearly black; slightly hydrated phosphoric oxide is next added in small quantities at a time, the mixture being still well cooled, and finally the compound is extracted with ether. The ether is then distilled off, and the residue mixed with cold water; the resulting white powder is washed with a small quantity of cold water. The compound is a powerful reducing agent, and behaves as a ketone with phenylhydrazine, hydroxylamine, and hydrogen cyanide. The author is further investigating the properties and constitution of the product in question.

8. "*The Inertness of Quicklime.*" By V. H. Veley.

The conditions under which calcium carbonate is formed from lime and carbon dioxide have been investigated by Debay, Raoult, and Birnbaum, with Mahn: but the experiments of these authors are neither described in detail, nor were they made under comparable conditions.

The experiments recorded in the paper were conducted on a much larger scale than heretofore, and the amount of combination between the lime and carbon dioxide as dependent on the conditions (1) of moisture, (2) of temperature, is investigated. It is shown that the combination is incomplete, not only with lime to which 11 per cent of water is added, but even with the hydrate; the presence of 10 per cent free water in the hydrate increases the absorptive power nearly fourfold. Dry carbon dioxide combines with lime to a slight extent at 300°, to a greater degree at 350°, and fairly completely at 420° (melting point of zinc; *cf.* Birnbaum and Mahn).

The conditions of the formation of calcium sulphite from lime and sulphur dioxide have been studied by Birnbaum and Wittich, who do not, however, give any quantitative results.

It is here shown that lime and sulphur dioxide, when dry, begin to combine at about 300°, and more completely at 352°; but at a higher temperature the resulting sulphite is decomposed into sulphate and sulphide, and by the interaction of the latter and the sulphur dioxide sulphur is formed.

There is a great similarity in the behaviour of dry carbon and sulphur dioxide as regards the amounts of them absorbed by lime under the same conditions of temperature. Incidentally it is noted that quicklime does not absorb nitrous fumes at ordinary temperatures.

It is proposed to continue these investigations.

9. "*The Products of the Interaction of Tin and Nitric Acid.*" By C. H. H. Walker.

This investigation is a continuation of the investigations of Veley on the conditions of the interactions of metals and nitric acid.

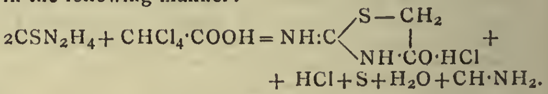
Since the work was commenced, a paper by Clemente Montemartini on the same subject has appeared.

It is generally stated in manuals on chemistry that metallic tin dissolves in nitric acid, forming both a stannous and stannic salt, according to the conditions of temperature and concentration of acid, but it does not appear that this statement is based on quantitative investigations.

In the paper determinations are given of the amounts of stannous salt formed according to the conditions of (1) mass of metallic tin; (2) temperature; (3) concentration of acid. It is shown that the proportion of stannous salt formed is but little affected by the mass of tin, and in the case of dilute acids by increase of temperature, but with more concentrated acids the effect is more marked, so that an alteration of a few degrees reduces the amount of stannous salt to *nil*. Increase of concentration of acid, other conditions remaining the same, decreases the proportion of stannous salt. The white, or yellowish white, substance deposited from fairly concentrated solutions is a hydrated stannic nitrate of rather indefinite composition (*cf.* Clemente Montemartini). The average value of a number of analyses corresponding most nearly with a formula $Sn(NO_3)(OH)_3$. The substance appears to slowly decompose on exposure, so that the composition varies not only with the time elapsing between its production and analysis, but also according to the method of purification adopted to eliminate nitric acid.

10. "*Interaction of Thiourea and some Haloid Derivatives of Fatty Acids.*" By Augustus E. Dixon, M.D.

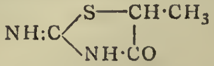
On warming thiourea with dichloracetic acid, either alone or in solution (in water or in dilute spirit), hydrogen chloride is evolved, sulphur and thiohydantoic acid are deposited and the filtered solution on standing yields orthorhombic crystals of thiohydantoin hydrochloride. The formation of this latter substance may be expressed in the following manner:—



$$2CSN_2H_4 + CHCl_4{\cdot}COOH = NH{:}C\begin{cases} S - CH_2 \\ \quad\quad | \\ NH{\cdot}CO{\cdot}HCl \end{cases} + \\ + HCl + S + H_2O + CH{\cdot}NH_2.$$

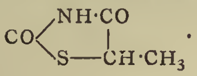
In the case of trichloracetic acid, complete decomposition occurs, carbonic anhydride, hydrogen chloride, hydrogen sulphide, sulphur, and chloroform being produced. Ethylic trichloracetate in boiling alcoholic solution has scarcely any action.

α-Monochlor- (or brom-) propionic acid and thiourea readily interact, yielding the hydrochloride (or hydrobromide) of methylthiohydantoin,



$$NH{:}C\begin{cases} S - CH{\cdot}CH_3 \\ \quad\quad | \\ NH{\cdot}CO \end{cases}$$

The latter compound, separated from its salts by caustic alkali, crystallises from alcohol in brilliant, vitreous prisms; it melts at 205°—206° (uncorr.), but is decomposed. It is not desulphurised, either by treatment with silver salts or with alkaline lead solution; on boiling with baryta-water it yields methylthioglycollic acid. On boiling with chlorhydric acid, ammonium chloride is produced, together with a substance crystallising in needles; this was not obtained in a pure condition, but from the mode of production, and the ready manner in which it undergoes conversion into methylthioglycollic acid, it must be $\beta$-methyldioxythiazole,



## NOTICES OF BOOKS.

*A Manual of Dyeing.* For the Use of Practical Dyers, Manufacturers, Students, and all interested in the Art of Dyeing. By Edmund Knecht, Ph.D., F.I.C.; Christopher Rawson, F.I.C., F.C.S.; and Richard Loewenthal, Ph.D. Vol. II. (Second Notice). London: Charles Griffin and Co., Limited.

In this volume the authors consider the artificial organic colouring matters, arranged in the following groups:—Direct cotton colours, basic colours, acid colours, eosins and rhodamines, mordant colours, and miscellaneous group, comprising aniline-black and, among others, indigo.

In the first group figures *Erika*, which, we submit, might more fittingly be written *Erica*. The direct cotton colours are in many cases inapplicable on account of their liability to bleed.

The basic colours are so named because their chromophorous group is contained in the bases. Their tinctorial power is in many cases exceptionally high. It is satisfactory that the authors are able to affirm that in the manufacture of magenta the arsenical process has been to great extent relinquished in favour of nitrobenzene process.

The acid colours are sub-divided into three groups: the nitro-compounds, the azo-compounds, and the sulphonated basic colours. The eosins and rhodamines are distinguished for remarkable brilliance, and are, in solution, more or less fluorescent. In some cases their fluorescent character is an objection, and they are for many purposes too fugitive and too expensive.

The mordant colours dye fibres only with the aid of metallic mordants. Their type is alizarin, and the important process of Turkey-red dyeing turns on its use.

In the history of aniline-black the part taken by Lightfoot scarcely comes into sufficient prominence.

As regards the manufacture of artificial indigo it is admitted that Bayer's expectations have not been realised, and that there is little demand for propiolic acid. Whether Heymann's method of manufacturing artificial extract of indigo—which the authors call indigo carmine—will prove successful the future must show..

The machinery used in dyeing forms the subject of an elaborately illustrated section.

Of no less importance is a part devoted to experimental dyeing, which is especially necessary in case of novel colours.

Concerning the recognition of the fastness of colours to light, we find some very appropriate remarks on the discrepancy of results obtained by different experimentalists, and some suggestions are thrown out relating to a uniform procedure.

The analysis and valuation of dye wares are very fully and ably treated. For most wares comparative dye tests are still almost the only method available. It is admitted, however, that the colorimeter will often be found very useful in the examination of dyes as a check upon the dye tests. For indigo, chemical analysis is pronounced necessary.

"The experimental error involved in making dye tests is great in comparison with that of an ordinary chemical analysis. Let the conditions be ever so favourable, the eye is incapable of discriminating between two shades of the same colour if the difference is less than a certain small amount which in a chemical analysis would be considered great." It was hoped that the spectroscope would have supplied us with a physico-chemical means of deciding on the value of colours, but so far this expectation has not been fulfilled.

Vol. III. contains the colour patterns in illustration of the text. They may fairly be pronounced excellent. The work of Messrs. Knecht, Rawson, and Loewenthal will prove a boon to all persons concerned with the tinctorial industries, and we feel sure that it will be widely appreciated.

## CORRESPONDENCE.

### PURIFICATION OF WATER USED FOR STEAM-BOILERS.

*To the Editor of the Chemical News.*

Sir,—I shall consider it a great favour if you will insert in your next issue the following reply to some observations made on our Water Purification Process by R. Jones, Ph.D., in the Chemical News, vol. lxvii., pp. 171 and 185.

I note that the absolute reliability and automatic action of our process, which is used to satisfaction all over the Continent in over four hundred works is not contested. Dr. Jones contends, however, that the possibility of a slight excess of free alkali increased by concentration may be very detrimental to the boiler, and in support of this assertion he enumerates several instances in which boilers are said to have been attacked by the presence of free alkali in the feed-water. We must strongly protest against this possibility for the following reasons:—

A very bad water may require as much as 300 grms. of caustic soda per cubic metre, and if we suppose that on account of variations in the composition of the impure water as much as 10 per cent of the alkali should go undecomposed into the feed-water, it would represent an addition of 0·00003 per cent; and if we take it that this amount of free alkali is increased by concentration tenfold, we should still arrive at a homœopathic dilution. It is easy and inexpensive enough to blow off the boiler occasionally in order to avoid even this possible concentration.

For this reason we need not enlarge upon the question which still seems open to slight doubt: Whether or not iron plates are very slightly attacked in the long run by a concentrated boiling solution of alkali? We are fully acquainted with the observations which have led some people to the wrong conclusion of some boilers being attacked. The boiler plates, when the boiler has been fed for some time with very bad water, and covered with incrustation, are subject to considerable overheating, which causes rivets and bolts to loosen. The tightening of the joints is, however, very effectually done by the incrustation, so that these defective places remain unobserved by the stoker.

If such a boiler is properly knocked out and cleaned before the application of our system, and the small amount of incrustation in the joints gets gradually dissolved, the boiler is bound to leak. After all, this proves nothing but that before the wholesome application of a reliable water purification plant, the boiler should be closely inspected and repaired.—I am, &c.,

C. Harzer,
Representative of A. L. G. Dehne,
Halle on Saale.

Billiter Bldgs., Billiter St,
London, E.C.

## DANGEROUS TRADES.

*To the Editor of the Chemical News.*

Sir,—An article on this subject in the Chemical News, vol. lxvii., pp. 179 and 203, leads me to enclose you some paragraphs from a paper I have lately published on the subject of the methods used in Germany for the protection of the workpeople. I should be glad if you could find space for them.—I am, &c.,

M. Carey Lea.

The first step taken in Germany was to appoint Commissions which investigated all the dangerous trades and reported very fully on the evils found and their remedies. The entire empire was then divided into fifty-one districts, for each of which a competent inspector was appointed. These inspectors have a right to examine every part of all the factories and workshops, and to require the establishment of all such reforms as they judge necessary. They confer not only with the employer, but with the workmen. A few instances will serve to show the beneficial effects which have resulted from this system.

In the district of Alsace-Lorraine 663 factories were inspected, out of which 286 were reported as having insufficient ventilation. Out of these 286 factories 209 were for textile industries. Much improvement was being made by the adoption of the system of ventilating with warm and moist air. The introduction of electric lighting has done much to improve the atmosphere of the workrooms.

In the manufacture of mirrors great improvement in the health of the workpeople has been brought about by the use of silver instead of mercury for coating glass. In the town of Furth the mirror factory is reported as using silver exclusively for the mirrors sent to North America, and for about two-thirds of its entire product. At this factory the number of days of illness caused by mercurial poisoning in 1885 was 4074; in 1889 it was 1003. In 1890 this was reduced to 148, and since May, 1890, there have been no cases at all. When the serious nature of mercurial poisoning is considered, the great improvements brought about partly by the use of a less poisonous metal and partly by better methods, can be understood.

In the district of Cassel-Baden the manufacture of chrome gave rise to sickness among the workpeople. By improved methods the number of sick days was reduced in one year from 2865 to 899, so that at present the time lost by sickness by those actually engaged in the factory barely exceeds the proportion of loss among the outdoor workmen, masons, carpenters, laborers, &c.

In the great lead works at Tarnowitz, in the district of Oppeln, efforts have been made to check the malignant lead poisoning caused by the escape of lead fumes. This has been done by connecting all the different furnaces with a powerful ventilator, which draws out the fumes by exhaustion and forces them into a tall chimney. Arrangements are also made for purifying the gases from the lead which they contain. The effect of these changes on the health of the workpeople has been very remarkable. The number of sick days has been reduced to one-sixth of what it was formerly.

In the manufacture of phosphorus matches, the cases of constitutional injury by phosphorus poisoning have been very greatly reduced in number.

The manufacture of mineral fertilisers is attended with danger in all cases where the phosphate rock contains fluor-spar. Such rock when treated with sulphuric acid disengages vapours of hydrofluoric acid which are very injurious to the lungs and also destructive to vegetation. At a factory in the district of Breslau-Liegnitz this danger is completely overcome, and even a profit is made, by bringing the hydrofluoric vapours into combination, and thus obtaining artificial cryolite.

The fouling of streams by the drainage of factories is in all manufacturing districts a source of much trouble. The chemicals used are for the most part injurious to the water in every way, rendering it unfit for drinking, and tending to destroy all animal life contained in it. As a single example it may be mentioned that it has been ascertained by actual trial that one part of burnt lime introduced into 100,000 parts of water in a river is sufficient to kill all the fish contained in it.

Stringent measures have been taken in Germany to diminish this evil, though in some cases, and particularly in the manufacture of beet-sugar, it has proved very difficult to find effectual means. But by the use of chemicals it can be accomplished. The Strobnitz factory, which works up 70,000 tons of beets each season, and whose waste-water amounts to over 1000 gallons per minute, purifies this so thoroughly that a specimen taken by the inspector remained three weeks in a warm room odourless. In some cases it has proved that waste-waters containing organic matter which were very injurious to streams by reason of the fermentation which they set up, were found, on the other hand, very useful to fertilisation by means of irrigation. For example, a starch factory on the River Werra caused much damage by fouling the water with the waste products of the manufacture. But when these products were carried to the neighbouring farms their fertilising qualities proved so valuable that the demand for them could hardly be met.

These facts, all derived from official sources (the reports of the inspectors epitomised in the *Chem. Zeitung*), serve to show what valuable reforms can be effected through the agency of intelligent inspection.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 18, May 1, 1893.

**Determination of the Specific Heat of Boron.**—Henri Moissan and Henri Gautier.—The mean specific heat of boron between 0° and 100° is found experimentally as 0·3066. This figure is higher than that of Weber. The difference goes on in the same direction up to the temperature of 234°. The value 0·3066 thus obtained, if multiplied by the atomic weight of boron, 11, gives the result 3·3 in place of 6·4, the figure admitted by the law of Dulong and Petit. This atomic heat increases with the temperature, and if we extrapolate the above results up to a temperature of 400°, we find for the atomic heat a figure close upon 6·4.

**Rock Phosphates of Animal Origin, and on a New Type of Phosphorites.**—Armand Gautier.—The author has analysed the deposits found in the Department Herault, and finds them similar to phosphorites, hitherto found only in certain islands of the Caribbean Sea.

**Sanitary System adopted by the Hygienic Conference at Dresden.**—M. Brouardel.—The delegates propose to lay an embargo upon rags, old clothes, and dirty linen coming from suspected territories. Portugal, Greece, and Turkey, however, adhere to the old system of quarantine.

**Researches to Determine Bases for a New Method of Detecting the Sophistication of Butters by Margarine, whether used alone or in a Mixture with other Fats, Animal or Vegetable.**—A. Houzeau.—The substance of this bulky paper will be inserted as early as possible.

**Densities and the Molecular Volumes of Chlorine and Hydrochloric Acid.**—A. Leduc.—It appears to the author that if we compare the molecular volumes of any two gases under normal conditions, the one which is nearest to its critical point must have the smaller volume.

**Decrease of the Coefficient of Expansion of Glass.**—L. C. Baudin.—If we consider a thermometer uniformly heated in all its parts, the capacity of the stem diminishes uniformly in the same proportion as the volume of the bulb. To the decrease of the capacity of the thermometric channel there corresponds a proportional contraction in the length of the stem. If, with M. Benoit, we accept 0·000021552 as the coefficient of the cubic expansion of green glass, it becomes about 0·00002096 after re-heating, having raised the zero by 26·2°.

**Decomposition of Oxalic Acid by Ferric Salts under the Influence of Heat.**—Georges Lemoine.—The phenomena depend on the decomposition of ferric salts by water as established by Debray and Berthelot. A solution of ferric oxalate, if heated to 100°, is slightly decomposed. $Fe_2O_3$, momentarily soluble, is set at liberty, reduced by oxalic acid, and yields $CO_2$. If there is an excess of oxalic acid, it interferes with the decomposition of the ferric salt, and consequently the final reaction, producing $CO_2$. The extensive alteration of ferric chloride by water is the turning-point of all these reactions.

**Contribution to the Study of the Leclanche Battery.**—A. Ditte.—This memoir is not suitable for useful abstraction.

**Alkaline-Earthy Fluorides.** — C. Poulenc. — The author has examined the strontium, barium, and calcium fluorides. He has studied the action of gaseous hydrofluoric acid upon strontium chloride, the action of alkaline chlorides upon amorphous strontium fluoride, that of the hydrofluoride of potassium fluoride upon amorphous strontium fluoride, and that of strontium chloride upon potassium fluoride hydrofluoride. Crystalline strontium fluoride forms regular octahedral crystals.

**Determination of Phosphoric Acid.**—A. Villiers and Fr. Borg.—This paper will be inserted in full.

**On Licarene, derived from Licareol.**—Ph. Barbier.—Licareol is transformed by loss of water into the cyclical hydrocarbonated group, $C_{10}H_{16}$, when the dehydration is effected by means of acetic anhydride, and into $C_{10}H_{18}Cl_2$, if it takes place under the influence of dry, gaseous hydrochloric acid. The carbide, $C_{10}H_{16}$, is an active limonene, whilst the compound $C_{10}H_{18}Cl_2$ is its inactive hydrochlorate.

**On a Vegetable Nucleine.**—P. Petit.—The nucleine which the author has extracted from barley differs from the animal nucleines of Kossel, Liebermann, and Bunge, by containing no sulphur. In solutions of common salt it swells up and becomes greyish. It does not give Millon's reaction, and is soluble in alkalis. If heated under pressure with water (four atmospheres) it dissolves to a pale yellow liquid, which is a very favourable medium for microbia. The author suspects the presence of a compound analogous to this nucleine in the black matter of the soil.

**Periodicity of the Odoriferous Property in the Fatty Series.**—Jacques Passy.—The variations of the odoriferous power point to a more complex law than the author had at first suspected. With the fourteenth term of the series of fatty acids the odour reaches the limits of perceptibility *for us*.

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### *Zeitschrift fur Analytische Chemie.*
### Vol. xxxi., Part 6.

**Preparation of Absolutely Pure Hydrogen Peroxide.**—Léon Crismer.—(From the *Bull. Soc. Chim.*).

**Preservation of Normal and Decinormal Oxalic Acid.**—R. W. Gerland.—(From the *Journ. Soc. Chem. Industry*).

**The Colouration which Sodium Hypobromite Assumes if kept in some Glass Bottles.**—G. Denigès (*Journ. Pharm. Chimie* and *Chemiker Zeitung*).—The author found that such a solution quickly lost its golden yellow colour in a reddish brown glass. He observed that this change of colour is due to the presence in the glass of manganese, which is converted into an alkaline permanganate. The hypobromite is still fit for analytical uses.

**On Rare Earths.**—Lecoq de Boisbaudran (*Bull. Soc. Chim. de Paris*).—Already inserted.

**Determination of Iron in Ferric Salts.**—Alonzo C. Campbell. — (From the *Journal of Analytical Chemistry*).

**Volumetric Determination of Mercury.**—Rodolfe Namias (*Gazz. Chimica* and *Chem. Zeit.*).—The mercury must be present as chloride or be transformed into this state. The solution of mercuric chloride is mixed with a solution of stannous chloride until all the mercury is thrown down as mercurous chloride. As indicator the author uses a freshly-prepared solution of sodium molybdate, with which filter-paper is moistened. The latter turns blue on spotting with the solution of mercury in question as soon as a slight excess of stannous chloride is present. The solution of stannous chloride is prepared by dissolving from 2 to 3 grms. of pure tin in hydrochloric acid and diluting to 1 litre. The standard is ascertained with solution of iodine, or, preferably, with from 0·2—0·4 grm. pure mercuric chloride, which is dissolved in 50 c.c. water and 0·5 c.c. hydrochloric acid.

**Separation of Mercury from the Metals of the So-called Arsenic and Copper Group.**—K. Bülow.—(An Inaugural Dissertation).—Already inserted.

**Determination of Phosphoric Acid by the Molybdenum Method.**—O. Foerster (*Chem. Zeit.*).—In the method in question, the complete washing of the ammonium-magnesium phosphate is very difficult, as both the precipitate and the filter retain traces of ammonium molybdate with great obstinacy. Further, the impurity which almost always appears as a slight turbidity of the liquid on dissolving the ammonium phosphomolybdate in ammonia passes into the precipitate on throwing down the magnesium ammonium phosphate in the cold. These defects, according to Foerster, may be almost entirely avoided if the ammoniacal solution of the ammonium phosphomolybdate is gently heated before adding the magnesia mixture. The precipitate is then crystalline, much less bulky, and can be easily thrown upon the filter, so that it is much more easily washed. The impurity which occasions a turbidity on dissolving the ammonium phosphomolybdate in ammonia does not pass into the precipitate, and on washing runs through the filter. In order to throw down small quantities of ammonium-magnesium phosphate, which may remain in solution on precipitation in heat, the liquid when cold is once more thoroughly stirred up before filtration. For washing the precipitate it is convenient to use a solution of ammonium nitrate (50 grms. in 1 litre of liquid ammonia at 2·5 per cent). The residue on ignition is then almost white.

**Volumetric Determination of Bromine along with Chlorine and Iodine.**—Norman McCulloch.—(From the Chemical News).

**Determination of Sulphur in Iron and in the Sulphides Decomposable by Hydrochloric and Sulphuric Acids.**—L. L. de Koninck and Ed. Dietz.—(From the *Revue Universelle des Mines Metallurgie*).—Already inserted.

**Determination of Sugar.**—A series of extracts from the *Zeit. Angew. Chemie*, the *Chemiker Zeitung*, the *Journ. Anal. Chemie*, the *Bull. Soc. Chim. de Paris*, and other journals.

**Determination of Glycerin in Wine.**—B. Proskauer.—This paper will be inserted in full.

**Occurrence of Boric Acid in Caustic Alkalies.**—F. P. Venable and J. S. Callison.—(From the *Journ. Anal. Chem.*).

**Preparation of a very Efficient Platinum Black.**—O. Loew (*Berichte Deutsch. Chem. Gesellschaft*).—The author dissolves 50 grms. platinum chloride in water so as to make up from 50 to 60 c.c., and mixes it with 70 c.c. of a 40 to 45 per cent formaldehyd. In the mixture he dissolves 50 grms. caustic soda and adds an equal weight of water. The greater part of the metal is at once deposited. After twelve hours the mixture is filtered through a suction-filter, when a yellowish liquid passes through the filter and on boiling deposits a little platinum. A part of the precipitate dissolves on washing as soon as the salts are chiefly removed, forming a deep black solution. The washing is therefore interrupted until the incipient process of oxidation is completed. Oxygen is freely absorbed, and the temperature rises from 36° to 40°, whilst a crackling sound is heard and small gas-bubbles escape. The platinum black, thus rendered loose and porous, is completely washed, pressed, and dried over sulphuric acid.

**Action of Sublimate upon Zinc.**—H. Börnträger (*Pharm. Central Halle*).—A development of hydrogen much accelerated by means of platinum chloride is at once arrested if one or two drops of a 10 per cent solution of mercuric chloride is added to the sulphuric acid in contact with the zinc. The mercury nitrates do not interfere with the development of hydrogen.

**Sensitive Turmeric Paper.**—According to the *Bolletino Farmaceutico* a very sensitive paper is obtained by dipping slips of neutral filter paper in a solution of tincture of turmeric (1 : 7). When quite dry they are steeped in 2 per cent potassa-lye and quickly washed with pure distilled water. The papers when dry are packed up in tin-foil. This paper reacts with 1 part of hydrochloric acid in 150,000 parts water.

**Preparation of a very Sensitive Indicator from Litmus.**—J. Lüttke (*Apoth. Zeitung*).—The author extracts 100 grms. commercial litmus three or four times successively with warm water, and evaporates the united extracts down to 200 c.c. The concentrated solution is acidified with 20 c.c. of hydrochloric acid at 25 per cent and dialysed through parchment paper until all the acid is eliminated. The residual colouring-matter is remarkably sensitive. A drop of decinormal alkali produces in 100 c.c. of water mixed with this colouring-matter an instantaneous and sharply marked blue colouration. A drop of a decinormal acid produces an equally sharp change. On precipitating the concentrated solution with alcohol, and drying the precipitate, we obtain a preparation which may be kept for a long time unaltered.

**Analysis of Commercial Aluminium.**—A. Rössel (*Schweiz. Wochenschrift* and *Chemiker Zeitung*).—The impurities, chiefly iron and silicon, greatly interfere with the value of the aluminium. The author gradually introduces from 3 to 4 grms. aluminium into about 35 c.c. of hot potassa-lye at from 30 to 40 per cent. The metal dissolves, leaving a black, flocculent residue. It is supersaturated with pure hydrochloric acid in a platinum capsule without previous filtration and evaporated to dusty dryness. The mass is then moistened with hydrochloric acid, and the silica is determined in the ordinary manner. For determining the iron the author also uses from 3 to 5 grms. aluminium, dissolves as above, mixes with an excess of dilute sulphuric acid, heats until the solution is clear, and titrates with permanganate. Great care must be taken that the potassa-lye is free from silica.

**On Glucinum.**—Gerhard Krüss and Hermann Monath (*Ber. Deut. Chem. Gesell.*).—The authors discuss the opening up of glucinum minerals, the preparation of glucina and metallic glucinum, as also the behaviour of glucina as a feeble acid and with feeble acids.

## MEETINGS FOR THE WEEK.

Tuesday, 23rd.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
Wednesday, 24th.—Geological, 8.
Thursday, 25th.—Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.
— Institute of Electrical Engineers, 8.
Friday, 26th.—Royal Institution, 9. "The Imaginative Faculty in its relation to the Drama," by H. Beerbohm Tree.
— Physical, 5. "Discussion upon Dr. Lodge's paper, "The Foundations of Dynamics." "A New Photometer," by A. P. Trotter. "Notes on Photometry," by Prof. S. P. Thompson, F.R.S. Exhibition of a Vibrating Bar, by C. J. Woodward.
Saturday, 27th.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

Errata.—P. 178, in the Table, Series 6, Valence VIII., *for* "Tr" *read* "Ir." Also erase the first half of Series 1 and the last half of Series 7.

THE CHEMICAL NEWS.

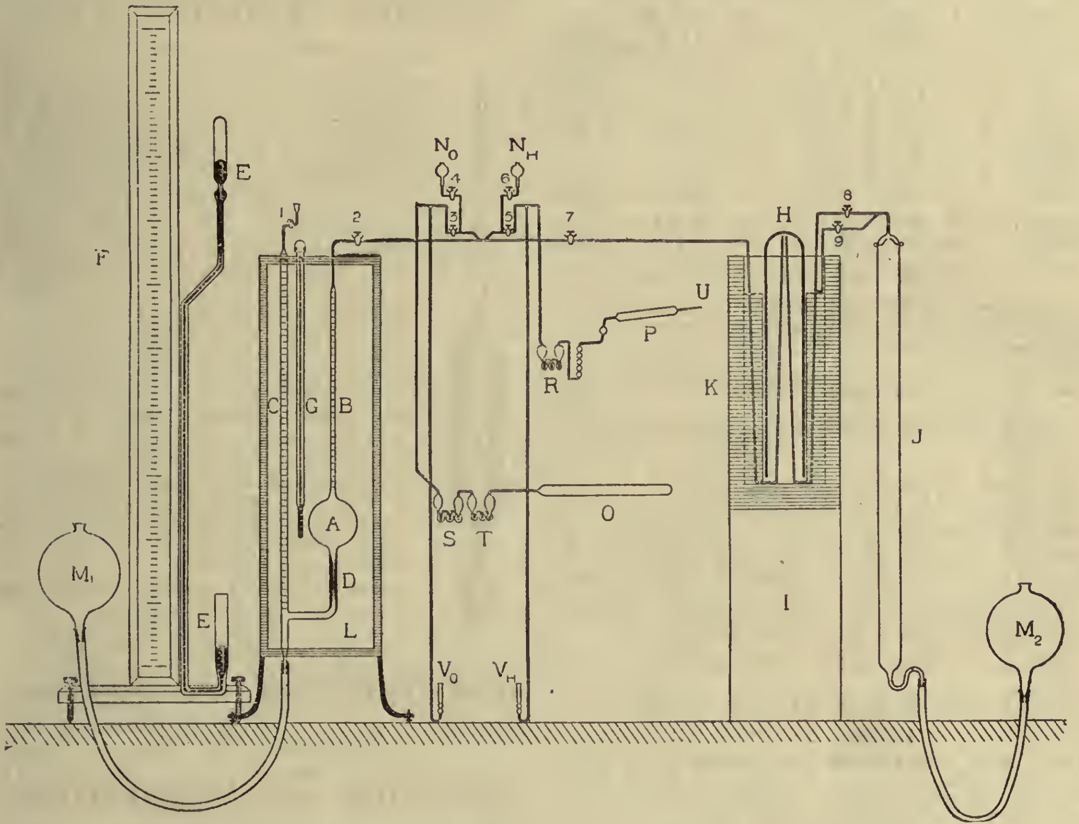
Vol. LXVII., No. 1748.

### ON THE
## COMPOSITION OF WATER BY VOLUME.*

By ALEXANDER SCOTT, M.A., D.Sc.,
Jacksonian Demonstrator in the University of Cambridge.

In a preliminary note presented to the Society in June, 1887, the results of twenty-one experiments on the composition of water by volume were given in detail. The ratio deduced from these experiments was less than two volumes to one of oxygen. This result was unexpected, because of the greater compressibility of oxygen than of hydrogen, but as every one of the experiments pointed to this result, the evidence for it seemed conclusive. Pursuing the investigation with improved apparatus, especially as regarded making a complete analysis of the residual gas, a serious source of error was discovered in the use of any combustible lubricant for the taps employed. On substituting syrupy phosphoric acid for the vaseline previously employed, the oxides of carbon disappeared as ordinary impurities. In the latter experiments two forms of apparatus were employed, the chief difference being that in the earlier form the measuring vessel was not of fixed volume, so that both volume and pressure of the gas had to be measured; in the later form the gas was measured at constant volume by varying the pressure, which alone, therefore, required measurement in each experiment.

As in the apparatus formerly used, the entire apparatus could be completely exhausted of air before beginning an experiment by using the mercury reservoir ($M_1$) and the measuring vessel as a Toppler's pump. The gases were measured in A and B, and after measurement were mixed in the jar, H, whence they were drawn into the explosion tube, J, and then exploded in fractions till all was used up. The residue was now passed back into H, and then into B, and there measured, re-transferred to J, and expelled through the tap 9 into an absorption tube, and analysed with potassium hydrate and pyrogallol for carbon dioxide and oxygen, and for gases not absorbed by these reagents. These gases were most probably nitrogen, hydrogen, and carbon monoxide (from the absorbents). The mixture thus obtained gave at any rate a *maximum* value for any impurity in the gases employed; when it fell below 1/110,000 the gases were considered pure.



The hydrogen required was made from—

1. Electrolysis of dilute sulphuric acid.
2. ,, ,, hydrochloric acid.
3. Action of steam on sodium.
4. Palladium hydride.

The oxygen was obtained from—

1. Re-crystallised potassium chlorate.
2. Mercuric oxide.
3. Silver oxide.

All the results in which potassium chlorate was used as the source of the oxygen gave low results, doubtless due to traces of chlorine accompanying the oxygen even

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* Abstract of a Paper read before the Royal Society.

after passing through potassium hydrate. The best oxygen was obtained from silver oxide, and the best hydrogen from palladium hydride. The palladium used combined with enough hydrogen to perform twelve experiments in succession. The results of the last series are given in the following Table. The oxygen required was obtained from silver oxide.

Column A contains number of experiment.
,, B contains date of experiment.
,, C contains measured volume of hydrogen in grms. of mercury.
,, D contains measured volume of oxygen in grms. of mercury.
,, E contains excess of hydrogen in grms. of mercury.
,, F contains excess of oxygen in grms. of mercury.
,, G contains impurity in grms. of mercury.
,, H contains number of volumes of hydrogen which unite with one of oxygen.

| A. | B. | C. | D. | E. | F. | G. | H. |
|---|---|---|---|---|---|---|---|
| XXV. | Ap. 1 | 6863·8 | 3443·8 | — | 15·4 | 0·3 | 2·0020 |
| XXVI. | ,, 1 | 6870·0 | 3432·9 | — | 2·1 | 0 | 2·0024 |
| XXVII. | ,, 2 | 6870·1 | 3439·7 | — | 9·2 | 0 | 2·0026 |
| XXVIII. | ,, 4 | 6848·7 | 3422·1 | — | 2·9 | 0 | 2·0030 |
| XXIX. | ,, 4 | 6792·5 | 3386·6 | 13·5 | — | 0 | 2·0022 |
| XXX. | ,, 5 | 6809·2 | 3399·5 | 1·5 | — | 0 | 2·0025 |
| XXXI. | ,, 6 | 6793·9 | 3399·6 | — | 7·7 | 0 | 2·0029 |
| XXXII. | ,, 6 | 6789·6 | 3389·5 | 2·9 | — | 0 | 2·0023 |
| XXXIII. | ,, 7 | 6808·5 | 3396·4 | 6·0 | — | 0 | 2·0028 |
| XXXIV. | ,, 8 | 6793·1 | 3395·8 | — | 2·1 | 0 | 2·0017 |
| XXXV. | ,, 8 | 6786·5 | 3395·0 | — | 5·4 | 0 | 2·0022 |
| XXXVI. | ,, 9 | 6814·8 | 3411·9 | — | 9·3 | 0 | 2·0028 |

Mean = 2·00245 ± 0·00007.

The mean of all the experiments in the variable volume apparatus, and in which potassium chlorate was the chief source of oxygen, is—

2·000903 ± 0·00004 impurity equally distributed in both gases,
1·99925 ± 0·00005 impurity assumed to be all in hydrogen,

in five series of nineteen experiments in all.

The mean of all the experiments in the constant volume apparatus, in which silver oxide was used as the source of the oxygen, and sodium and steam either directly, or after absorption in palladium for the hydrogen, is—

2·002435 ± 0·00006 impurity in both gases equally,
or 2·002431 ± 0·00006 ,, hydrogen alone.

This is the mean of fifty-three experiments in five series.

If six experiments be rejected we get the value—

2·002466 ± 0·000003

as the result of forty-seven experiments in five series, and any impurity makes no difference, whether it be assumed all in the hydrogen or equally distributed in both gases. The most probable value, however, is 2·00245.

This value, combined with the value 15·882 for the ratio of the densities found by Lord Rayleigh, gives for the atomic weight of oxygen—

15·862.

| | |
|---|---|
| Dittmar and Henderson's value is .. .. | 15·866 |
| Cooke and Richards's value is .. .. .. | 15·869 |

Leduc (*Comptes Rendus*, cxv., 313) found for the ratio of the volumes, by taking the density of electrolytic gas from strong potassium hydrate solution and his own values for the densities of hydrogen and oxygen,—

2·0037,

and for the ratio of densities—

15·905,

giving for the atomic weight of oxygen—

15·876.

Morley's experiments (*Amer. Journ. Sci.*, xli., 220, 276) are objected to on the ground that his apparatus is too complicated, his measuring vessel far too wide for accurate measurement, and to its being used also as the explosion tube, the transferring of his gases from one mercury trough to another, and his giving no means of saturating the gases with aqueous vapour. He further measures his pressures to 1/200th of a m.m. His ratio for the volumes is given as—

2·00023,

or only 1/10th of the difference from 2·0 exactly of that found by the above-described experiments.

## IMPROVEMENTS IN THE MANUFACTURE OF BORAX.

By H. N. WARREN, Research Analyst.

Boracic, or boric acid, as is well known, is one of the feeblest acids to be met with, being readily replaced by all other known acids, and even in some respects by carbonic acid; but, on the other hand, viewing it as an anhydride, we find it standing foremost, and at elevated temperatures even slowly replacing such acids as phosphoric and sulphuric acids.

Boric anhydride is, in fact, when pure almost entirely fixed at the most elevated temperatures obtainable. A tared platinum crucible containing an ounce of the substance which had been exposed to a full white heat for over two hours, was found after weighing to have lost in weight but 5 grains. The peculiar properties of the acid, however, are vastly different, volatilising readily upon the application of heat, insomuch that it is practically impossible to distil a solution containing boracic acid without a portion passing into the distillate. Again, if boric acid is melted at a low red heat in a platinum or other suitable vessel, as long as aqueous vapours are discharged, volatilisation of the boron present is perceptible until about 70 per cent of the water present is discharged, the remaining portion of the water being expelled in an almost pure condition.

Taking advantage of these properties, the author has devised a method by which the production of borax is brought about by subjecting common salt (sodium chloride) to the action of the crude boracic acid of commerce aided by superheated steam, the decomposition being effected by employing large clay retorts, composed for the most part of acid resisting material, the tops being tubulated to allow of the introduction of the steam required during the reaction. The retorts being charged with an intimate mixture consisting of well ground salt and boric acid, the neck of the retort being connected with a refrigerator for the purpose of condensing the acid thus obtained.

Directly the retorts assume a low red heat, hydrochloric acid is disengaged in abundance. The heat is now slightly raised, and the supply of steam so regulated that water in the form of steam is allowed to enter through the tubulure in sufficient quantity to condense the hydrochloric acid formed in connection with the refrigerator; the result being a speedy and complete decomposition of the salt employed, with the production of anhydrous borax, which remains in the retorts, whilst a dense and pure acid collects from the condenser.

When the reaction is terminated, the contents of the retorts, consisting of anhydrous borax, is ejected, whilst still red hot, into cold water, where it is allowed to remain for forty-eights hours, during which time it will have passed into solution, from which, by the ordinary routine of crystallisation, it is obtained as ordinary commercial borax.

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## ON THE ABSORPTION-SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Continued from p. 232).

The substituted chloracetic acids were now used as solvents for chromium hydroxide to see if they also yielded similar absorption-spectra.

The chromium hydroxide was the same as that used in the previous experiments. It was digested with strong aqueous solutions of the acids at the ordinary temperature, and the solutions thus obtained were examined by the spectroscope as soon as possible, as the acids, under the circumstances of the experiment, are liable to decomposition. The results are not so satisfactory as one would wish, for the absorption-bands are characterised by their indefiniteness, and they are therefore extremely difficult to measure. Another curious characteristic is that these solutions are all of a distinctly blue colour by daylight, although the specimen of chromium hydroxide from which they were made was the same as was used in the fatty acid experiments, in which case the solutions are green. The mono-chloracetic acid solutions are of course decomposed on heating and become green. The absorption-spectrum also alters, and is similar to that given by a solution of chromium hydroxide in glycollic acid. The same is true if the solutions be kept for some time.

The following are the measurements actually obtained by dissolving chromium hydroxide in the following acids.

*Monochloracetic Acid* (17).—Continuous absorption to 740; shadow to 710; then a very faint band from 698 to 686. The broad absorption from 655 to 504, and continuous absorption from 480.

*Dichloracetic Acid* (18).—Continuous absorption to 740; shadow to 721; then a very faint indefinite band from 689 to 681. The broad absorption from 655 to 513, and continuous absorption from 480.

*Trichloracetic Acid* (19).—Continuous absorption to 740; shadow to 714; a very faint indefinite band from 701 to 674. The broad absorption from 655 to 509, and continuous absorption from 480.

These substituted fatty acids, then, do not behave to chromium hydroxide as do the fatty acids themselves, as the absorption-spectra given by the former when they are treated similarly are of an entirely different character. Further, the successive replacement of hydrogen by chlorine appears to move the absorption-band in the red part of spectrum nearer its more refrangible end.

It was thought advisable to compare the spectrum of chromic chloride itself with the above, as it appeared not unlikely that the chloracetic acids might form this compound under the conditions of the experiment, and as it is well known, a solution of chromium chloride gives an indefinite absorption-band in the red part of the spectrum.

Two distinct specimens of chromium chloride were made, as was also a specimen of the colloidal chromic chloride. The same specimen of chromium hydroxide used in the former experiments was dissolved in hydrochloric acid and its absorption-spectrum examined.

Two specimens of chromium chloride were made from the metal.†

(I.) By dissolving the metal in hydrochloric acid.

(II.) The metal was carefully washed with dilute acid for six hours and then washed with water, and the residue dissolved in hydrochloric acid.

All these specimens gave the same absorption-spectrum (29):—Continuous absorption to 717; a very faint indefinite band 704 to 689; a shadow at 653 joining broad absorption from 619 to 550, and continuous absorption from 472.

This absorption-spectrum is very similar to that given by chromium hydroxide dissolved in monochloracetic acid. But it can be shown that the bodies are not identical, for on heating the monochloracetic acid solution—owing to decomposition—it yields a totally different absorption-spectrum, while the chromic chloride is not influenced by heat.

*Colloidal Chromium Chloride* (30).—This was made in the usual way, by dialysing as neutral a solution as possible of chromic chloride. After some months the colloidal chloride was obtained as a solution of a fine green colour, which could be easily gelatinised on the addition of sodium chloride. The absorption-spectrum of the colloidal solution was similar, but not identical, with that given by the chloride solution. In the case of the colloidal chloride the absorption-band in the red part of the spectrum was distinctly nearer the less refrangible end of the spectrum.

The measurements are as follows:—

Continuous absorption to 800, with a shadow to 750. An indefinite band from 710 to 695. Then a shadow at 665 joining broad absorption from 621 to 544, and continuous absorption from 480. The significance of this absorption-spectrum will be discussed later.

*Tribromacetic Acid* (20).—Chromium hydroxide is very slightly soluble in a strong aqueous solution of this acid. The absorption-spectrum is similar to that given by trichloracetic acid, but the absorption-band in the red part is moved still nearer the more refrangible end of spectrum. The measurements in a layer of the solution 3 c.m. thick are: Continuous absorption to 770; a faint band from 676 to 668; a shadow at 653 joining the broad absorption at 610 to 534, and continuous absorption from 459.

*Glycollic Acid* (21).—This acid dissolves chromium hydroxide easily, yielding a solution having a bluish green colour by daylight and a red colour by lamplight. The absorption-spectrum is as follows:—

Continuous absorption to 758. Then two bands in the red 723 to 714, and 706 to 695 respectively. Then a sharp shadow at 670, which joins the broad absorption from 644 to 507, and continuous absorption from 473.

*Lactic Acid* (22).—This acid easily dissolves the chromium hydroxide. The solution was green by daylight and red by lamplight. The absorption-spectrum given was similar in character to that given by the preceding acid.

The absorption-bands are very indefinite, and their edges indistinct, so that the same difficulty in measuring them was experienced. The absorption-spectrum is as follows:—Continuous absorption to 770. Two very faint and indistinct bands at 721 and 707 respectively. Then a somewhat more definite and broader band at 676—665. Then the broad absorption from 629 to 533, and continuous absorption from 467.

The bands 721 and 707 seemed to be moved towards the less refrangible end of the spectrum than is the case in glycollic acid. But the apparent movement is slight, and the bands indistinct, so that it is impossible to speak with certainty.

*Trichlorlactic Acid* (23).—A saturated solution in cold water was made of this acid, and the chromium hydroxide dissolved in the cold in it. The solution was red by daylight as well as by lamplight. The absorption-bands in this case are also very indistinct, but after repeated measurement they appear to be as follows:—Continuous absorption to 721. Two faint bands at 710 and 674

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* *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

† Obtained from E. Merck, Darmstadt.

respectively. A shadow at 655 joining broad absorption from 610 to 526, and continuous absorption from 483.

These measurements point to the absorption-bands being moved slightly towards the red end of the spectrum as compared with lactic acid.

*Phosphoric Acid* (24).—Chromium hydroxide was dissolved in an excess of this acid, producing a fine green coloured solution, which gave an absorption-spectrum which is somewhat remarkable. It is as follows:—Continuous absorption to 740. Then a band in the midst of partial absorption at 698—686. Then a space free from partial absorption. Then a band at 670—650, another band at 639—621 and partial absorption to 585, and finally continuous absorption from 471.

The notable point of this absorption-spectrum is that there is so little absorption in the green part. In this respect the phosphoric acid solution is different from all the other salts of chromium examined, with one exception, potassium chromicyanide.

*Malic Acid* (25).—A strong aqueous solution of this acid easily dissolves chromium hydroxide. The solution is bluish-red by daylight and red by lamplight, and gives the following absorption spectrum.

Continuous absorption to 729. Then a band at 707 to 695. A deep shadow at 670 which joins the broad absorption at 644 which ends at 498, and continuous absorption at 480.

*Tartaric Acid* (26).—The absorption-spectrum of a solution of chromium hydroxide in this acid is known, as it has been mapped by Th. Erhard (*loc. cit.*).

My measurements are:—Continuous absorption to 800. A very indefinite band at 707—695. A shadow at 668 which joins the broad absorption at 639 which ends at 501, and continuous absorption from 475.

*Citric Acid* (27).—A strong aqueous solution of this acid, when used as a solvent for chromium hydroxide, gives an absorption-spectrum very similar in character to that given by the two previous acids. The following were the measurements obtained:—

Continuous absorption to 736. A faint band at 707 to 698. A shadow at 660, which joins the broad absorption at 629, and which ends at 504. Then continuous absorption from 467.

*Isethoinic Acid* (28).—A 50 per cent aqueous solution of this acid was used to dissolve chromium hydroxide, which it did without difficulty. The colour of the solution was bluish green by daylight and red by lamplight. The absorption-spectrum was as follows:—

Continuous absorption to 717. A very indefinite band at 695—668. The broad absorption at 653—506, and continuous absorption from 480.

The absorption-spectra of the foregoing acids are characterised by the indefiniteness of the absorption-bands in the less refrangible parts, and they fade off so gradually on both sides that it is extremely difficult to measure them.

The close resemblance of these absorption-spectra, together with the great differences of molecular complexity of the acids used as solvents, suggested the probability of the absorption-spectra given being produced mainly by chromium hydroxide or oxide, and not to the combination of this body with the acids used as solvents.

It is well known that chromium hydroxide is not precipitated by caustic alkalis in presence of certain organic bodies, as sugar, tartaric acid, &c. Some experiments were made with this view. Solutions of chromium hydroxide in citric and tartaric acids were made, and a slight excess of caustic potash was added, and the absorption-spectrum observed. These solutions gave the same absorption-spectrum, which is as follows:—

Continuous absorption to 721. A faint band at 710 to 692. A shadow at 665 joins the broad absorption at 617, which ends at 547. And continuous absorption from 473. Ammonia solution was substituted for caustic potash, but the resulting absorption-spectrum was the same as the above.

In another set of experiments the chromium salt was varied; chromium chloride and sulphate were used together with strong aqueous solutions of cane sugar, glycerin, and tartaric acid respectively. Slight excess of caustic potash was added in one case, and an excess of ammonia solution in the other. The absorption-spectra in all these cases did not differ from the one given last.

Chromium hydroxide itself dissolves in an excess of caustic potash; this also gave the same absorption-spectrum as the above, and, lastly, freshly precipitated chromium hydroxide, precipitated by caustic potash and suspended in water, gave exactly the same absorption-spectrum (31).

There can be no doubt, then, but that the above is the absorption-spectrum given by chromium hydroxide, and as was to be expected it agrees exactly with that given by a solution of colloidal chromium chloride, and also fairly well with the absorption-spectra given by citric, tartaric, and malic acids.

It would therefore seem probable that in these cases and probably in others the acids have no power in modifying the absorption-spectra, which therefore must be produced either by chromium hydroxide or oxide existing in the various solutions examined.[*]

It is further to be noticed that the band 710—692 of chromium hydroxide is represented in most of the chromium salts examined; a glance at Table I., column 2, will render this evident. Sometimes it occurs as a broad band, as in the case of chromium chloride; sometimes as a faint, thin, incidental band, as in the fatty acid series; and sometimes as a thin, sharp, and exceedingly dark band, as in the case of the chromoxalates; while in the substituted chlor-acetic acids it is somewhat moved towards the more refrangible end of the spectrum.

(To be continued).

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# A REVISION OF THE ATOMIC WEIGHT OF BARIUM.[†]

## First Paper: The Analysis of Baric Bromide.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 233).

### *The Choice of Material.*

It has been already stated that the most satisfactory determinations of the atomic weight of barium have had baric chloride as a starting point. In many respects this substance is well adapted for the purpose; but one serious cause of error must be carefully guarded against in the usual method adopted for its analysis. The well-known solubility of argentic chloride influences the accuracy, not only of the weight of chloride obtained, but also of the apparent end point of the precipitation after the method of Gay Lussac. Long ago Stas[‡] pointed out this cause of error, and carefully described his method of procedure, that others might correct his results if they were found to be based upon an incorrect assumption. He added an excess of silver to the chloride to be investigated, and then added the standard solution of a chloride until no more cloudiness was observable. Such a method under ordinary circumstances requires from two to eight m.grms. less of silver to correspond with a given weight of chloride than would be required if the solutions were added in the inverse order.

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[*] Since the above work was done, Recoura (*Comptes Rendus*, cxii., 1439) has shown by thermic methods that a green basic sulphate—$2Cr_2O_3.5SO_3$—exists in solution when the blue sulphate is converted by heating into the green salt, and also that this salt is unable to fix a further quantity of acid.

[†] *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

[‡] Aronstein's translation of Stas's Memoir, pp. 46, 56, 59, and especially 295 (Leipzig, 1867).

A number of years afterward* Stas changed his method of procedure, and selected the point half-way between the two extremes as the true end point of the silver reaction. He gave reasons for this change of view, but wholly ignored his previous results. Commentators have laid hardly enough stress upon this important difference between the two series of determinations, although it necessarily involves an error in one series or the other.

Working before even the earliest date of Stas's publication upon this subject, the experimenters upon the atomic weight of barium naturally overlooked the whole question. As nearly as may be guessed from their incomplete accounts, they usually selected the end point obtained by gradually adding argentic nitrate to baric chloride; hence their results cannot be compared with either of Stas's series.

Much time during the past eighteen months has been spent upon this question. The investigation of baric chloride showed that results for the atomic weight of barium varying from 137·35 to 137·50 might easily be obtained from the purest possible salt, according to the interpretation of the data. At last a definite conclusion was reached, and the work is now nearly ready for publication.

The necessity for some other basis for the atomic weight of barium early led to the search for a new starting point. In the course of this search most of the available baric salts were investigated with regard to their adaptability for the present purpose.

Baric nitrate holds water with great obstinacy, and no certain point of constant weight could be reached by gradually heating it. Besides, the only two methods available for its analysis are extremely unsatisfactory. The conversion into the chloride is rendered very difficult because of the insolubility of both the nitrate and chloride in strong acids. The complete conversion of the nitrate into the sulphate is also difficult, because of the well-known occlusion of one salt by the other. Moreover, supposing the analysis by either method to have been satisfactorily performed, the data furnished would give only the worst possible foundation for the calculation of the atomic weight of barium (see Ostwald, *Allgemein. Chem.*, i., 23). Many qualitative and quantitative experiments led to the complete rejection of baric nitrate as the material for analysis.

Baric bromate is very readily prepared in a pure state by a few successive crystallisations, and it was hoped that this salt would furnish especially valuable testimony upon the case. But investigation showed that it was impossible to be certain that the crystallised salt did not contain an excess of occluded water. Upon the other hand, it is doubtful if all the water of crystallisation can be expelled without a slight decomposition of the salt. Since water is the one impurity most to be dreaded in all such work, baric bromate was rejected, except as a means of obtaining the bromide in a pure state.

The carbonate was next experimented upon, and, while the results were more promising than those from the nitrate and bromate, they were less satisfactory and conclusive than those obtained from baric bromide.

The advantages of the use of a bromide for an investigation upon atomic weights are so manifest, and have been so often discussed, as to need no further mention. The current descriptions of the deliquescence and instability of the baric salt alone postponed the consideration of this substance. Investigation showed that misleading statements about the salt have found their way into chemical literature. In reality, the substance is as well adapted for accurate work as baric chloride and most other materials upon which we must rely.

(To be continued.)

## THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 177).

PARRY determines the small percentage of carbon in very soft steels by the method of combustion in vacuum. The dry carbonaceous residue obtained by any of the usual methods, *i.e.*, by digestion with copper sulphate or chloride, &c., is mixed with excess of pure copper oxide, previously ignited in a vacuum to remove all gaseous matter and moisture. The moisture is transferred to a porcelain tube closed at the end, and the tube nearly filled with copper oxide. The tube, &c., is attached to the Sprengel mercury air pump, exhausted, and allowed to stand for one hour; if no leakage occurs, a full red heat is applied by any convenient means—preferably a small gas combustion apparatus—for one hour. Carbonic acid is freely evolved, and is pumped into a tube graduated in 1-10th c.c. attached to the pump. The gas is accurately measured with the usual precautions, and the percentage of carbon calculated therefrom.

Very close results may thus be obtained, and a very minute quantity of carbon may be estimated with certainty. (For details and full description of apparatus see Blair's iron and steel analysis). This method at first sight may seem too elaborate and complicated for ordinary work, but our experience is to the contrary. Once the apparatus is in complete working order, combustion may be made with great facility. The same tube and copper oxide may be used repeatedly if the precaution be taken of keeping the tube, &c., always attached to the pump, and slightly heating and pumping just previous to use.

### *Graphite.*

For the determination of this constituent four or five grms. of the metal are dissolved with the aid of a gentle heat in hydrochloric acid, the residue collected on an asbestos filter similar to that employed for the collection of the carbonaceous residue in the estimation of total carbon, washed with hot water, a solution of caustic potash, alcohol, and a little ether. The residue is then dried, mixed with copper oxide, burnt in a stream of oxygen,† the resulting carbonic acid being collected and weighed.

This method furnishes very accurate results, but is rarely employed, the graphite being determined either in the case of silicon previously dealt with, or preferably by the method now described, which yields results sufficiently accurate for all technical purposes. Five grms. of the sample, contained in a beaker, are digested at a gentle heat, with 60 c.c. of dilute hydrochloric acid, and when the solution is nearly complete, 20 c.c. of the strong acid is added and further digested. Dilute the resulting solution with a large volume of water, collect the residue composed of graphite, &c., on a *weighed* filter paper, wash well with water, a dilute solution of hydrochloric acid, and a solution of caustic potash, to remove silicon, and finally to remove hydrocarbons, with alcohol and ether. The filter paper and contents are then transferred to a water oven, dried at 100—120° C., and weighed. As the graphite thus obtained may still contain small quantities of silicon, &c., in the form of slag, it is placed in a platinum crucible, ignited at a strong heat, the residue weighed and deducted from the original weight of the graphite, and if required the percentage of slag thus obtained tabulated. Analysts do not usually give determinations of slag and diffused iron oxide, but even for practical work these should always be estimated.

### *Sulphur.*

The methods employed for the determination of sulphur in iron and steel are based upon two principles, viz.:—

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* The Memoir was presented in 1876, according to the title page. *Mem de l'Acad. de Belg*, Nouv. Ser., xliii. See also Van der Plaats, CHEM. NEWS, liv., 52, 88.

* From *Industries*, April 4, 1893.

† For a description of the apparatus employed and manner of carrying out the combustion consult a work on organic chemistry.

(1) That upon treating the metal with an oxidising reagent, such as nitric acid or other oxidiser, the sulphur is oxidised into sulphuric acid, which is subsequently precipitated as barium sulphate ($BaSO_4$) with barium chloride. (2) The sulphur is evolved as sulphuretted hydrogen upon treating the iron or steel with sulphuric or hydrochloric acid. Of the two, we are of opinion that the method based upon principle (1) yields, in the hands of a skilful operator who rigidly observes the necessary precautions, the most accurate results, and, furthermore, that those obtained by the other methods should be checked by it.

The *modus operandi* of the method is as follows:—The filtrate contained in a beaker, remaining from the estimation of the silicon, or, if it has not been determined, that obtained upon dissolving 4 grms. (with sulphurous iron 2 or even 1 grm. is quite sufficient) of the sample in 60 c.c. of nitro-hydrochloric acid, with subsequent evaporation of the solution to complete dryness, re-dissolving in hydrochloric acid, and separation of the silica as previously described, is gently evaporated down to dryness. The beaker, &c., is allowed to cool, the contents moistened with a small quantity of hydrochloric acid, a gentle heat applied, and the solution again taken to dryness.

This operation is repeated until it is judged that the whole of the nitric acid is expelled. Finally, a small quantity of hydrochloric acid is added to the dry residue, and the solution evaporated until a crust commences to form on the surface, at which point it is arrested and the crust dissolved in three or four drops of hydrochloric acid. If these directions be strictly carried out, the solution will be free from nitric acid and nitrates, which are precipitated by barium chloride, as also from an excess of hydrochloric acid, which is essential for the obtainment of good results, barium sulphate being in our experience soluble to a slight extent in acid solutions of ferric chloride. The solution thus obtained is diluted with 700 c.c. of water, and the sulphuric acid contained in the same precipitated as barium sulphate ($BaSO_4$) by the addition of 5 c.c. of barium chloride (prepared by dissolving one part of the crystals in ten of water). After thoroughly mixing the solutions, cover the mouth of the beaker with a watch-glass and set aside to stand in a warm place for at least twelve hours, during which time the barium sulphate will be precipitated. At the expiration of that time syphon off as much as possible of the clear supernatant liquid, and throw the remainder, together with precipitate—removing the portions adhering to the sides, &c., of the beaker—on to a Swedish filter. Wash the filter and contents two or three times with a dilute solution of hydrochloric acid and thoroughly with hot water, transfer filter, &c., to a platinum or porcelain crucible, ignite at a bright heat, and when cold weigh the residual $BaSO_4$, every hundred parts of which correspond to 13·73 parts of sulphur.[*]

It occasionally happens that the precipitate, instead of being perfectly white, is of a pinkish tinge, due to the presence of iron, but the quantity is so small that it may be safely disregarded. If, however, it is a decided red, the precipitate contained in a platinum crucible is fused with six times its weight of sodium carbonate, the fused mass treated with a small quantity of dilute hydrochloric acid, the solution filtered, and the barium sulphate, now free from impurities, collected on a filter, washed, &c.

The methods based upon principle (2) are numerous, the majority being rapid and of easy execution. These advantages are, however, considerably lessened by the fact that they cannot be said to furnish absolutely accurate results on account of the probability of a proto-sulphate being retained in solution, likewise the insoluble matter *in some irons seems to retain* small quantities of sulphur. Neither can they be employed with all classes of iron, such as white iron. Where only approximate results are desired they furnish very fair results in a short time. In the method now described a metal is precipitated as sulphide from the solution of its salts by conducting the sulphuretted hydrogen evolved through. The absorbent employed is a solution of copper sulphate, prepared by dissolving 60 grms. of the crystals in a litre of water.

The details of the method are as follows:—In a small glass flask, A (Fig. 2), provided with a caoutchouc cork, through which a safety acid funnel, B, passes, reaching to nearly the bottom of the flask, and a tube, C, bent at right angles, welded to the neck, place 4 grms. of the sample, and in the glass cylinder, D, of 250 c.c. capacity, 220 c.c. of the copper sulphate solution. Arrange the apparatus over a gas-burner so that the tube, C, reaches inside nearly to the bottom of cylinder D, and through the funnel pour in some dilute sulphuric acid (one part acid to three of water) until the stem is immersed to a depth of half-an-inch. The acid immediately attacks the metal with evolution of sulphuretted hydrogen, &c., which makes its escape through the tube C into the copper sulphate, where as it ascends it is decomposed, the sulphur combining with the copper, forming a precipitate of copper sulphide (CuS), while the hydrogen is liberated. Towards the end, when the reaction becomes enfeebled, accelerate by applying a gentle heat under the flask. When all action is at an end, expel the gas remaining in the flask by pouring in through the funnel lukewarm water, taking care that it does not overflow into the copper sulphate solution. Remove A, rinsing into D any portions of the precipitate which may adhere to the stem of C, collect the precipitate on a filter, wash thoroughly with cold water, and convert into copper oxide (CuO) by ignition at a red heat, and weigh. The ignited precipitate of copper sulphide contains 40 per cent sulphur.

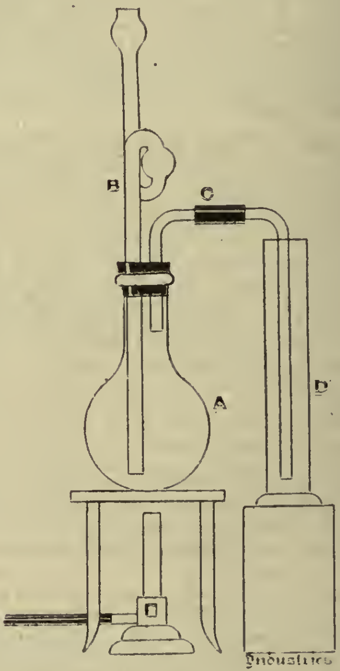

Fig. 2.

(To be continued).

**Production of the Sodium Light.**—H. Král (*Chem. Zeitung*).—The author uses asbestos rods saturated with common salt and prepared from asbestos paper. They are saturated by steeping in brine, and drying.

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[*] The principal objection to this method is that it is almost impossible to obtain $HNO_3$ and HCl acids free from $SO_4$.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, May 4th*, 1893.

Dr. Armstrong, President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Bateman, Saltney, near Chester; Robert S. Cahill, 90, Park Lane, Norwich; Alexander Mitchell Martin, Douglas Villa, Dunbeth Road, Coatbridge; Charles Alexander McKerrow, 41, Eccles Old Road, Pendleton, Manchester; William Ridgely Orndorff, Ithaca, N.Y., U.S A.; Wilfred Sessions, Russell House, Gloucester; Frank Ernest Thompson, 97, Murdock Road, Handsworth, Birmingham.

In answer to a question put by Mr. Cassal, the President expressed the opinion that to read the certificates of some without reading those of all candidates would be to make an invidious distinction, and that, therefore, if such a request were made, he should rule that it was out of order.

The following candidates were duly elected Fellows of the Society:—John Frederick Briggs, Julian L. Baker, William A. Bone, Laurence Augustus Baine, John Chas. Burnham, William Robert Burnett, Joshua Buchanan, Ralph Edward Brown, George Clayton, James Cameron, Harry Williamson Dixon, H. W. Dickinson, Robert Cecil Turle Evans, Thomas Edwards, Alfred Roland Gower, Robert George Grimwood, John Addyman Gardner, Hedley Gordon Jones, Hooper Albert Dickinson Jowett, Sorabji Manekji Kaka, Edmund George Lamb, Herbert Lloyd, Alan E. Munby, Henry John Monson, John Alan Murray, J. Frank McGregory, A.B., A.M., James Mason, Raffaello Nasini, William Henry Oates, S. Parrish, William Rintoul, James Henry Robbins, George Rudd Thompson, Frank P. Vandenbergh, B.S., M.D., A. F. Watson, John Wilkinson.

Of the following papers those marked * were read:—

*11. "*The Hydrates of Sodium, Potassium, and Lithium Hydroxides.*" By S. U. Pickering.

By cooling solutions of sodium hydroxide the author has succeeded in isolating a large number of hydrates in the solid crystalline condition. They considerably outnumber those of which he obtained indications by means of changes of curvature in the case of sulphuric acid—comparing similar ranges of strengths in the two cases—and hence no improbability can any longer be held to attach to these latter on account of their being so numerous.

The formula of the various hydrates isolated and their freezing points are as follows:—

| | Freezing-point. |
|---|---|
| $NaOH\cdot H_2O$ .. .. .. .. .. .. | 64·3° |
| $NaOH\cdot 2H_2O$ .. .. .. .. .. .. | 12·5 |
| $NaOH\cdot 3{\cdot}11H_2O$ .. .. .. .. .. | 2·73° |
| $NaOH\cdot 3{\cdot}5H_2O$ . .. .. .. .. .. | 15·55 |
| $\alpha NaOH\cdot 4H_2O$ .. .. .. .. .. .. | 7·57 |
| $\beta NaOH\cdot 4H_2O$ .. .. .. .. .. .. | − 1·70 |
| $NaOH\cdot 5H_2O$ .. .. .. .. .. .. | − 12·22 |
| $NaOH\cdot 7H_2O$ .. .. .. .. .. .. | − 23·51 |

The freezing-points or solubility curves of all these hydrates have been followed throughout considerable ranges; several of them—in one case as many as four—overlap each other. As it is scarcely possible to conceive that a crystalline hydrate can be extracted from a solution unless some molecules of that hydrate are present in the solution, this fact must prove that in some cases as many as four, probably even more, different hydrates exist in the same solution.

The existence of two different tetrahydrates is noticeable, as also is that of the complex hydrate of the formula $NaOH\cdot 3{\cdot}11H_2O$, or $NaOH\cdot 3H_2O + NaOH\cdot 4H_2O$, which is similar to two of the hydrates of which the author obtained indications in the case of sulphuric acid. Of the eight hydrates, that containing 3½ molecular proportions of water is the only one which has been previously described.

In the case of potassium hydroxide, two new hydrates—a mono- and a tetra-hydrate—have been isolated and examined, in addition to the already known dihydrate. The freezing-points of these are—

| | Freezing-point. |
|---|---|
| $KOH\cdot H_2O$ .. .. .. .. | 143° |
| $KOH\cdot 2H_2O$ .. .. .. | 35·5° |
| $KOH\cdot 4H_2O$ .. .. .. | −32·7 |

In the case of lithium hydroxide, the already known monohydrate was the only one obtained.

12. "*Detection of Arsenic in Alkaline Solutions.*" By John Clark, Ph.D.

The author shortly reviews the different methods by which arseniuretted hydrogen is generated in an alkaline solution, and finds, as pointed out by Hager, that Fleitmann's process, which depends on the interaction of finely-divided zinc and caustic potash, does not detect arsenic acid, but he is unable to confirm the statement of H. Fresenius, that Gatehouse's modification of Fleitmann's test indicates arsenic acid, as he has not been able to volatilise the slightest trace of arsenic by heating arsenate of soda with a large excess of pure aluminium and caustic soda, and he attributes the results obtained by Fresenius to the use of impure aluminium, or to the presence of arsenious acid in the arsenic acid. Experiments made to test the applicability of the Gatehouse process in estimating arsenic seem to show that, although it is very delicate and very convenient, it does give quantitative results, even when the whole of the arsenic is in the form of arsenious acid. He also finds that arsenic acid in an alkaline solution resists the action of sodium amalgam, and he concludes, therefore, that none of the methods which have been proposed for the generation of arseniuretted hydrogen in an alkaline solution detect arsenic acid.

13. "*Improvements in Reinsch's Process.*" By John Clark, Ph.D.

Reinsch's process, as carried out in the ordinary way, is capable of demonstrating the presence of very minute quantities of arsenic, and, according to Letheby, it withdraws every, and the smallest, trace of arsenic from organic mixtures, but there are two objections to its use in medico-legal cases.

1, When the quantity of arsenic is small, a stain is obtained which it is sometimes difficult to identify as arsenic, because the coated copper when heated is apt to give a layer of chloride of copper and organic matter, instead of arsenious acid.

2. It is not suitable for the quantitative estimation of arsenic, as it is not possible by means of heat to volatilise the whole of the arsenic from the copper.

The author's improvements consist in identifying the arsenic or antimony on the copper with greater certainty, and at the same time estimating the amount of each when they occur together. For this purpose he digests the coated copper in a cold mixture of dilute caustic potash and peroxide of hydrogen, which dissolves the arsenic and antimony, and converts them into arsenate and antimonate of potassium. The solution is then boiled, filtered, to get rid of the oxide of copper, evaporated to small bulk, and distilled with ferrous chloride and strong chlorhydric acid. The distillate is then saturated with sulphuretted hydrogen, and the arsenic weighed as sulphide, after being freed from traces of sulphur by washing with carbon bisulphide and alcohol. The residual liquid, from which the arsenic has been thus removed by distillation, is then tested for antimony.

### DISCUSSION.

Dr. BERNARD DYER drew attention to a remarkable difference in the results obtained on testing for arsenic by Marsh's process when the zinc used was in the shape of rods instead of being granulated. Some time since he had detected arsenic, not a mere trace, but a tangible, weighable quantity, in a certain pigment; but his results were disputed by the maker of the colour, who stated that a test made with rigid precautions by another operator had afforded no evidence of the presence of arsenic. The speaker had therefore met the other operator, and the following very curious results were obtained:—An ounce or two of his (Dr. Dyer's) highly purified granulated zinc was introduced into the Marsh apparatus, together with pure chlorhydric acid; at the end of an hour no appreciable deposit was formed in the heated tube, but on introducing 2 grms. of the pigment a dense arsenical mirror was soon obtained. The apparatus was then washed out, and charged with cast rod zinc, brought by the challenging operator; not only, however, was no deposit formed in the tube during the blank trial, but also on introducing 2 grms. of the pigment, no indication of the presence of arsenic was obtained, although the experiment was continued during an hour. Further experiments were made with this cast zinc, in which arsenious acid was deliberately added; when small fractions of a m.grm. were taken, and gas was slowly evolved, the arsenic was almost completely held back, and was but very partially deposited even when several m.grms. were taken, the results being altogether different from those obtained on using the granulated zinc. A number of samples of cast zinc were found to behave similarly. He had no doubt that some condition, probably of a physical kind, prevailed in cast zinc that did not prevail in the case of granulated zinc. The matter required further investigation, as it was one of obvious importance in toxicological work. There was little doubt that the arsenic is precipitated in the generating-bottle. Even granulated zinc produces some precipitation. It has been already shown that the frequently advocated use of platinum in the generating-bottle tends to hold back arsenic, and it seems probable that some couple may be formed in cast zinc.

*14. "*The Action of Light in Preventing Putrefractive Decomposition and in Inducing the Formation of Hydrogen Peroxide in Organic Liquids.*" By ARTHUR RICHARDSON, Ph.D.

It was shown in 1878 by Downes and Blunt (*Proc. Roy. Soc.*, xxvi., 488) that the development of bacteria and other putrefractive organisms is arrested under the influence of sunlight and oxygen; Janowski, Buchner, and Marshall Ward have recently made observations of a similar character. This sterilising influence of light in presence of oxygen has apparently always been regarded as the outcome of an action exercised within the organism; the author describes a number of experiments with urine, made with the object of ascertaining whether, when sterilisation has been effected by light, any oxidising agent, such as hydrogen peroxide, is formed, and whether such substance may not be the sterilising agent.

The method of testing is fully described, reliance being chiefly placed on the production of a yellow colour on the addition of a solution of titanic oxide in sulphuric acid; it is shown that this test affords a means of accurately estimating small amounts of hydrogen peroxide.

The author finds that, although no hydrogen peroxide is formed by the action of oxygen on sterilised urine in the dark, an appreciable amount is formed on exposing such urine to light, which is a proof that the production of the peroxide is not dependent on the presence of organisms. Urine in which bacteria have once flourished and which has then been sterilised at 100° no longer gives hydrogen peroxide on insolation.

Substances which destroy hydrogen peroxide were found to facilitate growth; thus, two portions of sterilised urine were exposed to light during several days, and to one of them was added a quantity of sterilised manganese dioxide; both were then placed in a dark cupboard: whereas both originally contained hydrogen peroxide, after twenty-four hours that to which no manganese peroxide had been added alone gave the yellow colour with titanic acid; and after fourteen days, fungoid growths had developed in the liquid containing manganese peroxide, while the other portion was still clear and contained hydrogen peroxide.

Experiments are described showing that if peroxide of hydrogen be added to fresh urine, this may be kept during a considerable period in the dark without the peroxide being entirely decomposed, and that its presence renders the liquid much less prone to undergo change under the influence of organisms, while, if added to urine in which fermentative change has already set in, it is rapidly decomposed.

15. "*The Supposed Saponification of Linseed Oil by Dutch White Lead.*" By J. B. HANNAY, F.R.S.E., and ARTHUR E. LEIGHTON.

Statements are quoted from technical writers showing the existence of a belief that white lead acts on the oil in which it is ground, and even indicating that the heat given out in mixing the pigment with oil is due to the occurrence of an interaction. The authors show that no heat is given out on mixing oil and white lead without undue friction, and that the heat observed in manufacturing operations is due to the conversion of the energy of the engine into heat by friction.

Also that white lead can be freed from oil as readily as any other pigment if a sufficient quantity be used, but it requires 100 c.c. to every grm. of pigment to effect a complete separation. Oleate of lead, whether basic, neutral, or acid, is shown to be readily soluble in ether, and it was mixed with white lead, both dry and ground in oil, and then extracted with ether, thus proving that if present it would certainly dissolve in the ether used to extract the oil. The method of testing is described, and it is shown that by passing sulphuretted hydrogen through the ethereal solution of the oleate, the faintest trace of oleate can be detected.

A series of tests carried out on samples of Dutch white lead produced by the most eminent makers is then described, and it is shown that no trace of oleate is present in any of them, nor does any insoluble organic compound cling to the lead after the oil is extracted. It is shown that normal carbonate of lead dissolves in heated oil more readily than hydrate, and that the hydrate is actually less acted upon at high temperatures than either Dutch white lead or normal carbonate, so that the hydrate does not saponify the oil.

It is shown that so small a quantity as 0·01 of oleate will seriously darken white lead when exposed to the air, and in presence of diluted sulphuretted hydrogen the smallest quantity of oleate causes the paint to darken when the pure white lead retains its colour, showing that the formation of a lead oleate would be deleterious.

### DISCUSSION.

Mr. HARLAND remarked that evidence of an action between linseed oil and white lead was to be found in the fact that it was impossible to wholly remove the oil from an ordinary white lead paint by means of ether.

Mr. BERTRAM BLOUNT said that the action between the linseed oil and white lead did not result in the saponification but in the oxidation of the oil, one of the products being "linoxin," which, though soluble in alcohol, was scarcely soluble in ether. This explained the fact alluded to by Mr. Harland. He took exception to Mr. Hannay's experiments, on the ground that he had used lead oleate, and not the lead linoleate which would result if any "saponification" occurred in linseed oil.

Mr. W. F. REID drew attention to the work of Mulder and Pettenkofer, which showed that no "saponification" was effected by dry white lead. It appeared that the white lead promoted slow oxidation of the oil and not "saponification."

The President said that he failed to understand the author's object in bringing such a communication under the notice of the Society. The statements made by the writers referred to could scarcely be taken seriously; such men would probably be unable to explain what "saponification" meant. No chemist would suppose that carefully dried white lead and oil, such as the authors used, would interact when carefully mixed, or that even carefully dried caustic soda would act under such conditions. It was apparently the universal belief that Dutch white lead had certain peculiar properties, but its effect was undoubtedly a complex one, in which probably not only the white lead and oil played a part, but also moisture, air, light, and time.

In reply, Mr. Hannay said that his experiments were made to refute the statement made in several technical manuals on paints.

(To be continued).

## PHYSICAL SOCIETY.

*Ordinary Meeting, May 12th, 1893.*

Prof. A. W. Rücker, F.R.S., President, in the Chair.

A paper on the "*Drawing of Curves by their Curvature*" by C. V. Boys, A.R.S.M., F.R.S., was read, and demonstrations of the method employed given.

Whilst giving a course of lectures on Capillarity in 1891, the author wished to explain the principles upon which the form of a water-drop depended; and finding Lord Kelvin's rule (*Proc. Roy. Inst.*, January 29, 1886) cumbersome, devised the modification now described. To apply Lord Kelvin's rule for drawing the generating curve of a capillary surface of revolution, the values of the expression—

$$\left(\frac{\delta}{a^2}+\frac{1}{\mathrm{OP}}+\frac{1}{\mathrm{NP}}-\frac{1}{\mathrm{N'P'}}\right)^{-1},$$

where PP′ is a short arc of a circle with centre O, N and N′ the points on the axis of revolution in which the lines OP and OP′ cut it, $\delta$ is the difference of level between P and P′, and $a$ a linear parameter, have to be calculated. Compasses are then set to this length, and another short arc, P′P″, drawn with centre O′ on the line P′N′, and the process repeated. This construction depends on the fact that the total curvature—

$$\left(\frac{1}{\mathrm{OP}}+\frac{1}{\mathrm{NP}}\right)$$

is proportional to the hydrostatic pressure at the point P, *i.e.*, proportional to the depth below the plane surface of the liquid. To avoid the trouble of finding reciprocals, a rule was divided so that the distance from what would be the zero of the scale are the reciprocals of the numbers attached to them, and the curvature of an arc, being the reciprocal of its radius, can be read off immediately by the rule. To meet cases where the curvatures of surfaces are in opposite directions, the zero, or ∞, is put at the middle of the rule and divided both ways.

The chief gain depends on the abolition of cumulative errors due to compass settings, which is effected as follows:—The rule is made of a thin slip of transparent celluloid with a small hole at the centre, or ∞. A small brass tripod, with needle feet, is placed so that two feet just penetrate the paper, and the third rests on the longitudinal straight line of the strip, which passes through the centre hole, thus forming a temporary but rigid centre about which the rule can rotate. A pen or pecil through the hole at ∞ traces out an arc whose curvature is equal to the reading of the scale where the needle point presses. When the rule crosses the axis of rotation of a generating curve, the numbers representing both curvatures are visible, and the position of the needle point corresponding to a given total curvature can readily be found. A small arc is then drawn. Holding the strip firmly on the paper the tripod is moved a little, so that the sum of the two readings at the needle point, and where the rule crosses the axis, has the value corresponding to the position of the tracing-point, and another arc drawn. Repeating the process a very perfect and accurate curve results. Details for drawing nodoids, unduloids, catenoids, and other curves, are given in the paper, and many beautiful examples which had been executed by Miss Stevenson were exhibited at the meeting. The author also pointed out that the locus of points about which the strip successively turns, is the evolute of the curve drawn by the tracing-point.

Prof. Perry considered the method a new departure of great value. When he (Prof. Perry) drew the capillary surfaces of revolution in 1875, he found that cumulative errors produced considerable discrepancies.

Prof. Henrici thought the method would be a very useful one.

Prof. Greenhill said one would now be able to secure better diagrams of transcendental and other curves than heretofore, and he thought Mr. Boys' method would supplant the laborious processes now used to determine the paths of projectiles. When the resistance varied as the square of the velocity, the elevation for maximum range depended on the initial velocity, and for a cube law, both elevation and range tend to finite limits as the initial velocity increases.

Prof. Minchin inquired whether the catenary could be best drawn by using a scale of equal parts instead of one divided reciprocally.

The President greatly appreciated the saving of labour effected by Mr. Boys' method, and thought the apparatus should be shown at the forthcoming Exhibition of Mathematical Instruments in Germany.

Prof. O. J. Lodge, F.R.S., read a paper on "*The Foundations of Dynamics*," in which he examines the objections raised by Dr. MacGregor (*Phil. Mag.*, Feb., 1893) against the views on "Newton's Laws of Motion and the Conservation of Energy," expressed by the author in 1885. The first part of the paper treats of the nature of axioms. An axiom or fundamental law is regarded as a simple statement suggested by familiar or easily ascertained facts, probable in itself, readily grasped, and not disproved, or apparently liable to disproof, throughout a long course of experience. On such bases the conservation of energy and of matter rest. Neither can be proved generally, but like other fundamental laws they fit into a coherent and self-consistent scheme, and are therefore worthy of acceptance until they are shown to be wrong.

The second part relates to the 1st and 3rd laws of motion. Dr. MacGregor objects to the 1st law on the ground that uniform motion is unintelligible unless its direction and velocity are specified with reference to a set of axes; and directly axes are introduced, difficulties occur as to their motion, because there is no satisfactory criterion of rest. Such notions the author deems artificial and unnecessary, except where it is required to define the absolute magnitude and direction of the motion. Reasoning from his own experiments he believed the ether was at rest, for he had not found it possible to move it by matter. The 1st law, he said, had been considered unnecessary as being only a particular case of the 2nd. While admitting the latter fact, he maintained that its separate statement was desirable, on account of its simplicity and its affording a practical definition of the mode of measuring time. As regards the 3rd law being deducible from the 1st, he pointed out that if it could be axiomatically asserted that the centre of mass of a rigid system moves uniformly unless an external force acts on the system, then the 3rd law follows. Newton apparently considered it best to state the 3rd law as an axiom, but to many persons it is not obviously axiomatic (some engineers do not accept it), hence its deduction from the other two laws is useful.

Part III. of the paper deals with the deduction of the law of conservation of energy from Newton's 3rd law, and universal contact-action. Dr. MacGregor objects to the author's definition of energy as the name given to "work done," and contends that this definition assumes conservation. On this point Dr. Lodge invited criticism, meanwhile pointing out that his definition was analogous to the customary definition of the potential function, and a name for the line integral of a force considered as a quantity that can be stored. On the basis taken, two bodies can only act on one another whilst in contact; hence, if they move they must move over equal distances. But their action consists of a pair of equal and opposite forces, therefore their activities are equal, and whatever one loses the other gains, *i.e.*, energy is transferred from one body to another without change in quantity. The law thus established, the author regards as more precise and definite than the ordinary law, because it implies not only the conservation but the identity of energy. The legitimate use of the phrase "potential energy" is discussed at some length, and the view that whenever energy is transferred it is also transformed, upheld.

In Part IV. the dissipation of energy, the nature of potential energy, and the 2nd law of thermodynamics, are considered. In discussing transference and transformation, "potential energy". is used to indicate the energy of a body under stress, and "kinetic energy," that due to sustained motion. Each corresponds to one of the factors of the product F $v$, "activity." So long as one factor is absent no activity can manifest itself; but directly the missing factor is supplied, transference and transformation begin. This was shown to hold in an example of an air-gun, with its muzzle plugged, chosen by Prof. MacGregor as an instance of transference of potential energy without transformation.

The law of dissipation of energy is stated thus:—"If a body has any portion of energy in such a condition that it is able automatically to leave the body, that portion usually does so sooner or later."

Instead of the ordinary form of the 2nd law of thermodynamics, the following statement is proposed:—"The portion of energy which a body can automatically part with is alone available for doing work."

In discussing this subject the author points out that the common notion that heat engines are much less efficient than water or electric engines is a mistake arising from the fact that in the one case the efficiency is calculated on the total energy, whilst in the latter cases only the available energy is considered.

Two appendices accompany the paper, one on the "Objectivity of Energy and the Question of Gravitation," and the other on "More detailed Discussion of the Transmission of Energy in Difficult Cases."

Prof. Greenhill said the paper was full of suggestive ideas. He could not agree with all the views expressed in the paper on the subject of Newton's 3rd law. In considering action and reaction as equal and opposite, Newton ignored the inertia of the medium, and if this be included, the forces are no longer equal.

Mr. Boys asked Prof. Greenhill if the first link of a chain pulled on the second link harder than the second pulled on the first?

Prof. S. P. Thompson thanked the author for getting rid of all square laws. He himself could not conceive of any effect being more than proportional to the cause.

Further discussion of the paper was postponed until next meeting.

**Quantitative Determination of Cholesterine.**—J. Lewkowitsch (*Berichte*) recommends Benedikt and Ullzer's method for ascertaining the acetyl number or the determination of the iodine number according to Von Hübl.

## NOTICES OF BOOKS.

*Seventh Annual Report of Her Majesty's Inspectors of Explosives:* being their Annual Report for the Year 1892. London: Her Majesty's Stationery Office.

It is most satisfactory to learn from this report that H.M. Inspectors of Explosives are still carrying out their duties successfully, and with an increased appreciation on the part of manufacturers, merchants, and the local authorities. It is here admitted that "there is no falling off in the high standard previously attained in the great majority of these establishments" (the manufactories of explosives), and that "the condition of the factories and magazines is now generally better than it was a year ago." It would even seem that more care and intelligence are now displayed by the workmen. This careless and obstinate neglect of precautions required by the law as well as by the factory regulations has been hitherto a danger not merely to the men themselves, but to all persons in the neighbourhood. Yet when a casualty has occurred a certain portion of the press has not scrupled to throw the blame upon the "cruel rapacity" of the masters who "compel" men to work under dangerous conditions!

Mischief occasionally still happens from miners having blasting powder in their houses and making up their own cartridges. Three miners in Northumberland have been convicted of this offence during the past year.

A welcome fact is that the quantity of gunpowder imported into Britain during 1892 has been smaller than in any year since 1879. On the other hand, our exports have reached a lower point than in any year since 1870.

Explosions of malicious origin have fortunately been rare in Britain. The worst case was that of the Walsall anarchists, convicted at Stafford Spring Assizes and sentenced to very inadequate terms of imprisonment.

We may here quote with approval an extract given from a pamphlet by Brigadier-General Henry Abbott, of the United States Army. He proposes that all persons guilty of outrages by means of explosives should, like pirates, be placed beyond the pale of the law, and should be at once hunted down in all civilised nations. "Recommendations to mercy" and verdicts of "extenuating circumstances" should, in their case, be prohibited.

After careful experiments, H.M. Inspectors have pronounced that arc lamps should in no case be used in a factory for explosives. Incandescent lamps should be protected by "at least one strong glass outer globe, so proportioned to the size of the lamp within that when the latter is burning under normal conditions the temperature of the outer globe shall not exceed 140° F."

No novel explosive of exceptionally remarkable properties has been introduced into manufacture in this country. No additional light has been thrown upon the nature of melinite, upon which our French neighbours rely for improving the Germans out of existence when the "war of revenge" breaks out. Had this compound been in course of manufacture by our authorities, every detail of its production would before this have become fully known to all our enemies, foreign or domestic.

Another source of public danger is too often ignored. Persons who may have been using "high" explosives sometimes carelessly leave cartridges, shells, &c., lying about. If such material falls into the hands of children or of criminals very serious results are probable. Of this not a few cases are here on record. Persons smoking whilst conveying ammunition imperil the lives of themselves and others.

A curious case seems to have occurred at New York:—"A labourer found a half-pound stick of frozen dynamite in a barrel of unslacked lime, just outside the pump-house, ane proceeded to smash it with a brick. The engineer coming on the scene, and observing the nature of the material, speedily retired to a safe distance, from which he directed the labourer what to do. Fortunately the dynamite did not explode; it was removed and taken out in a boat and dropped overboard. It is believed by the authorities that the dynamite was placed in the barrel by design." It was doubtless hoped that the moisture from the dynamite would slack the lime and cause an explosion!

The freezing of dynamite and the necessary thawing are abundant sources of accidents.

A very rare experience is that of a man who was blown to a distance of 120 feet by the explosion of a truck load of dynamite in consequence of a train leaving the metals. The man suffered no injury beyond a few bruises, though his clothes were entirely stripped off. The noise of this explosion, it is said, was heard to a distance of 35 miles.

Celluloid does not, in the opinion of H.M. Inspectors, come within the purview of the act, except made for use as an explosive. Moreover, it is not explosive, though certainly inflammable.

A doubtful case is recorded from Atherton, Lancashire. A man died, it is said, from inflammation of the brain resulting from the fumes given off on the explosion of a "roburite" cartridge. The case seemed chiefly to turn on the evidence of a local practitioner, who admitted that he had never heard of any similar case.

The list of authorised explosives is rather extensive. In many cases a chemist feels at a loss to account for the function of some of the ingredients.

The Inspectors certainly deserve great credit for the manner in which they are performing their duties.

*Experiments upon Magnesia, Alba, Quicklime, and other Alkaline Substances.* By Joseph Black, M.D., Professor of Chemistry in the University of Edinburgh, 1766—1797. Edinburgh: William F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1893. Small 8vo., 47 pp.

This little work, the first of the "Alembic Club Reprints," has a very laudable object. It is intended to "enable students of chemistry to possess themselves of a copy of this most important contribution to the foundation of chemistry as an exact science," and secondly, "to place within the reach of every student of chemistry a model of clear reasoning and of inductive investigation, second in this respect to nothing which has appeared in much more recent times."

The facts disclosed by Dr. Black have of course been the common property of chemists for upwards of a century. But as a model for the "researcher" the book retains its full value, and may be studied with much advantage.

In Dr. Black's writings, as in those of some others of our earlier men of science, there is a sobriety, an indisposition to outrun demonstration, which may indeed serve as a lesson.

It is mentioned in the preface that the orthography and punctuation of Black's original paper have been retained, and there follows the welcome announcement that Mr. Clay will publish reprints of other important writings of our earlier chemists.

**Detection of Phenols.**—L. M. A. Lambert (*L'Union Pharmaceutique*).—The author applies the colour reaction obtained on dissolving iodoform in the phenol in question and adding potassa lye. Ordinary phenol, resorcin, phloroglucin, and pyrogallol give a rose and red colour, orcine and salicylic acid a reddish violet, guaiacal and thymol a violet, hydroquinone and the naphthols a blue. For iodoform, chloroform or bromoform may be substituted. The reaction may be used inversely for the detection of small quantities of iodoform, chloroform, chloral, or bromoform, especially in toxicological investigations. The colours obtained as above disappear on the addition of an acid, but reappear on adding excess of alkali.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

### *Zeitschrift fur Analytische Chemie.*

Vol. xxxi., Part 6.

**Detection of Tubercle Bacilli in Sputum.**—P. Kaufmann (*Centralb. f. Bakt.* and *Chem. Centralblatt.*—The preparation fixed on the cover-glass in the usual manner, but in a very thin stratum, is stained with hot carbolic magenta and then moved up and down for three minutes in water at 98—99°, so that only a faint rosy reflection is visible on the preparation. By this treatment most bacteria are decolourised, whilst the bacilli of tubercle and leprosy resist the decolourising at least for a considerably longer time. On microscopic examination the bacilli of tubercle appear dark red on a whitish grey ground.

**Detection of Imitations of Amber.**— Otto Helm (*Industrie Blätter* and *Pharm. Central-Halle*).—Genuine Baltic amber, when polished, displays in polarised light between crossed nicols faint interference colours, rarely such as are brilliant. Copal is softer than amber, more soluble and more fusible. Gedanite (brittle amber) is distinguished from true amber (succinite) by the absence of succinic acid. Celluloid may be detected by its odour of camphor.

**Identity of Cystine and Ulexine.**—A. Partheil (*Archiv der Pharm.*). Cystine, $C_{11}H_{14}N_2O$, forms large, colourless, anhydrous, prismatic crystals, not deliquescent. It melts at 152—153°, and can be sublimed *in vacuo*. It is soluble in water, alcohol, chloroform, and acetic ether; less readily in benzol, amylic alcohol, acetone, commercial ether, and hot ligroin. In cold ligroin it is almost insoluble and quite insoluble in petroleum ether, carbon disulphide, and pure ether. The solution of cystine turns the plane of polarisation to the left. Its most sensitive reagent is potassium bismuth iodide, with which it yields a brown precipitate. If cystine or one of its salts is covered with the solution of a ferric salt, there appears a blood-red colour, which disappears on dilution with water or on acidulation. If a few drops of solution of hydrogen peroxide are added to the blood red liquid the colour disappears, but on gently heating on the water-bath is succeeded by a blue.

**A Reagent for Aloes.**—L. Schoutelen (*Oesterr. Ap. Vereines*).—A concentrated solution of borax produces in liquids containing aloes, on standing for 20 to 25 minutes, a green fluorescence, which disappears on long standing.

**Determination of Acetone in Urine.**—M. and A. Jolles (*Wien. Med. Wochenschrift*).—Acetone may be detected and estimated along with other volatile substances in the distillate with solution of phenylhydrazine. If acetone is present there is formed the corresponding phenylhydrazon, the quantity of which is determined according to H. Strache's process (*Monatshefte f. Chemie*).

**Detection and Determination of Sugar in Urine.**—E. Salkowski and M. Jastrowitz.—The authors have detected a new kind of sugar in the urine of a votary of morphine. With soda-lye and copper sulphate the urine gave a tardy but abundant precipitate of yellow cuprous oxide, but the fermentation test and polarisation gave negative results.

**A New Reaction for Glucose.**—O. Rosenbach.—On heating with alkali in a cold saturated solution of sodium nitroprusside, glucose and lactose give a deep brownish red or orange colour.

**Determination of Colouring Matter in Blood.**—F. Hoppe-Seyler (*Zeit. f. Physiol. Chemie*).—The author proposes a specially improved colorimetric process.

**Detection of Biliary Constituents in Animal Fluids.**—R. von Jaksch.—The author detects biliary pigments in the blood by allowing 10—15 cc. of the blood to coagulate, drawing off the serum with a syphon, filtering through a dense stratum of asbestos, and allowing it to congeal at 80° in a test-glass in the thinnest possible layer. Normal serum appears pale yellow and of a milky turbidity, whilst such as contains bile-pigment has a green colour.

**Determination of Peptones and Albumoses in the Contents of the Stomach.**—S. Riva-Rocei (*Centralblatt fur Klin Medicin*).—The author determines the total albumenoids by precipitation with absolute alcohol, drying and weighing; the coagulable albumenoids by Devoto's method, and the sum of the coagulable albumenoids and albumoses by saturating the liquid (previously acidulated, if necessary, with acetic acid) with magnesium sulphate, washing the precipitate with a solution of the same salt, drying at 110°, weighing, and incinerating. From the weight of the last precipitate he deducts the ash, with an addition of 15 per cent.

**Gutzeit's Arsenic Test.**—Curtmann (*Chem. Zeit.*).—There is danger that coal-gas present in the space examined may occasion a reaction, and that not every kind of paper is fit for use. Nagelfort (same journal) avoids this danger by causing the hydrogen to act upon finely pulverised silver nitrate placed between glass-wool in a U-tube. The slightest yellow arsenic reaction can easily be detected among the snow-white glass-wool.

**Elimination of Poisons in the Soil.**—F. Falk and R. Otto (*Vierteljahr. fur Gericht. Medicin und Sanitätswesen*) found that upon pouring solutions of alkaloids (1 per cent and 10 per cent solutions of stychnin and nicotin) upon soils, whether sandy or humic, there ensued a certain absorption of the poison or its transformation into harmless products. This action was decidedly stronger in humic soils, and feebler in sandy soils, but it was observed even in sterilised samples of soils, so that the decomposition of the alkaloids cannot be ascribed to the micro-organisms of the soil. The eliminating power of the soil is limited, and as soon as it is exhausted the alkaloidal solution passes through unchanged. Pure cultures of tetanus were rendered inert by passage through humus, but it is merely enfeebled by sand. In forensic chemistry the disappearance of alkaloids on filtering their solutions through soil is especially important.

**Fungus Poisons.**—Kobert (*Dorpat Naturf. Gesell.*, 1891).—No chemical details are given.

**New Reaction for Cocaine.**—Aloys Kuborne, jun. (*Pharm. Central Halle*).—A little cocaine is laid in a small porcelain capsule and covered with about 1 c.c. nitric acid of specific gravity 1·4, evaporated to dryness on the water-bath, cooled, and to the cold residue there is added a drop of alcoholic solution of potassa. No colour appears (distinction from atropin), but if the capsule is replaced on the water-bath there suddenly appears an intense violet colour.

**Poisonings with Strychnin and Brucin.**—Collin (*Pharm. Zeitung*) gives microscopic distinctions between the powders of the two seeds.

**New Determination of the Atomic Weight of Cadmium.**—H. N. Morse and H. C. Jones (*American Chemical Journal*).—The authors arrive at the value 112·0706 (O = 16).

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*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 8.

This number contains no original matter.

## MEETINGS FOR THE WEEK.

Tuesday, 30th.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.
— Society of Arts, 8. "American Silver Work," by Horace Townsend.
— Institute of Civil Engineers, 8. (Anniversary).
Thursday, June 1st.—Royal, 4.30.
— Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe LL.D.
— Chemical, 8. "Azo-compounds of the Ortho Series," by Prof. Meldola, F.R.S., and B. Burls. "The Fluoresceine of Camphoric Anhydride," by Dr. Collie. "The Action of Phosphoric Chloride on Camphene," by J. E. Marsh, M.A., and J. A. Gardner, M.A. "The Composition of Jute produced in England," by A. Pears, jun.
Friday, 2nd.—Royal Institution, 9. "Study of Fluid Motion by means of Coloured Bands," by Prof. Osborne Reynolds, F.R.S.
— Geologists' Association, 8.
— Quekett Club, 8.
Saturday, 3rd.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1749.

# ON THE ABSORPTION - SPECTRA OF SOME COMPOUNDS OF CHROMIUM.*

By W. LAPRAIK, Ph.D., F.I.C.

(Concluded from p. 246).

### *Absorption-Spectrum of a Solution of the so-called Perchromic Acid* (32).

It was thought to be of some interest to examine other compounds of chromium of a totally different constitution to the foregoing, in order to see how far their absorption-spectra differed from the previous compounds examined. With this idea in view, a solution of the fine blue coloured compound—the so-called perchromic acid—was prepared by the addition of hydrogen peroxide to a solution of chromic acid. I found the compound so unstable that I had great difficulty in making an observation; especially was this the case in solutions of such a degree of concentration as to give an absorption-spectrum in such thicknesses as 3 to 4 c.m. But by using a much more dilute solution, and increasing the thickness to about 10 c.m., I was able to measure the bands with the following result:—Continuous absorption to 740. Then two definite bands at 689—674 and 653—639 respectively. The broad absorption at 613—544 and continuous absorption from 448 (32).

In a thicker layer or a more concentrated solution, the two bands in the red join on to the absorption on either side, so that there is a narrow band of red light transmitted from 674 to 653; also the absorption in the green becomes somewhat broader while the blue light is transmitted.

This blue compound is known to be soluble in ether, but I found this solution so unstable that I was unable to make any measurements, but its absorption-spectrum appeared to be like the aqueous solution.

### *Some Salts of the Chrom-Ammonium Bases.*

I was fortunate in having placed at my disposal for the purpose of this research some specimens of salts of the chrom-ammonium bases. It was thought that it would be of considerable interest to spectroscopically examine these bodies, which differed so widely in chemical constitution from the compounds of chromium previously examined.

These salts have been the subject of several investigations by Jörgensen (*Journ. Prak. Chemie*, [2], 20, 105; [2], 25, 321; [2], 42, 206; [2], 44, 63).

Solutions of the salts were made in subdued light, and they were examined without loss of time, as it is known that light decomposes many of them.

### *Chloro-Purpureo-Chromium Chloride* (33 and 34), $Cl_2[Cr_2 10NH_3]Cl_4$.

This salt was first examined, a cold aqueous solution was made, and a layer 10 c.m. thick was used. This gave a continuous absorption to 695. Then a narrow band at 674, which has sharp edges, but it is not very dark; and then continuous absorption from 585 (33). By taking a thinner layer of solution—2 c.m. thick—the latter absorption was broken up. It began as a slight shadow at 545, and gradually reached a maximum at 474, where it stopped. But in the thinner layer the band 674 was no longer visible, and the continuous absorption was from 415 (34).

### *Xantho-Chromium Chloride* (35 and 36), $(NO_2)_2[Cr_2 10NH_3]Cl_4$.

An aqueous solution of this salt was made, and a layer of 15 c.m. thickness examined (35). It gave continuous absorption to 698. Then a narrow sharp band at 674, and then continuous absorption beginning with a shadow at 585, but dark at 572.

A thinner layer—2½ c.m.—splits up the latter absorption, which begins as a shadow at 544, then gradually reaches a maximum, and ending at 444, and the blue light which is transmitted is somewhat obscured. These effects are no doubt due to the presence of the $NO_2$ group in the salt. The narrow band 674 was again absent in the thinner layer, and the continuous absorption began at 414.

### *Rhodo-Chromium Chloride* (37 and 38), $(OH)[Cr_2 10NH_3]Cl_5+H_2O$.

An aqueous solution of this salt was made; it had a fine rose colour, and a layer of the solution of 15 c.m. thickness was examined, which gave continuous absorption to 740, with a shadow to 704; then a narrow, sharp, but not a dark band at 674; then two sharp lines, which are very close together, so that they are apt to be mistaken for a single band at 663 and 660 respectively; then a slightly thicker band, but not so dark and less distinct than the others at 650, and continuous absorption from 599. (37).

A thinner layer—2½ c.m. thick—gave continuous absorption to 800, with a shadow to 704. The four bands previously mentioned were not visible in this thickness, but the broad absorption was seen from 546 to 473, and continuous absorption from 413.

### *Leuto-Chromium Nitrate* (39), $[Cr_2 12NH_3](NO_3)_6$.

An aqueous solution of this salt having a thickness of 15 c.m. was examined. Its absorption-spectrum is quite different from the previous salts, and is as follows:—Continuous absorption to 701, which joins the first band at 683. Then follow three other bands, narrow and sharp, at 660, 650, and 631 respectively, the last being rather broader than the others; then a shadow at 599, which joins the continuous absorption at 536. (39).

In a thinner layer—2½ c.m.—of solution, all these bands fade out, and there is only continuous absorption from 510.

### *Chloro-Purpureo-Cobalt Chloride* (41).

A solution of this salt—15 c.m. in thickness—did not give any absorption bands, but only continuous absorption; but a layer of solution of 2½ c.m. thickness gave continuous absorption to 710, a broad absorption from 571 to 467, and continuous absorption from 414. This salt does not behave, therefore, like the salts of the chrom-ammonium bases, as it does not give absorption bands in the red part of the spectrum with the thickness of solution used.

It thus seems that the following compounds—chloro-purpureo-chromium chloride, xantho-chromium chloride, and rhodo-chromium chloride—all give the band 674 in layers of greatest thickness of solution. These salts all contain the radicle $[Cr_2 10NH_3]$, and it would therefore appear that this band is due to this radicle, for the compound leuto-chromium nitrate does not contain it, but the radicle $[Cr_2 12NH_3]$, and does not give the band referred to. Further, the bands 660 and 650 which occur in leuto-chromium nitrate appear also in exactly the same position in rhodo-chromium chloride. It is not quite evident from the usually accepted formulæ for these bodies why this should be the case, but it would appear that they have some part of their molecule of the same structure.

### *Some Double Cyanides of Chromium and Cobalt.*

*Potassium Chromi-Cyanide*, $K_6Cr_2(CN)_{12}$ (40).—An aqueous solution of this salt had a yellow colour in a layer of 15 c.m. thickness. It gave for the chromium

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* *Journ. für Prakt. Chemie*, xlvii., 305 (1893).

| | Continuous absorption. | 1. | 2. | 3. | 4. | 5. | Continuous absorption. |
|---|---|---|---|---|---|---|---|
| 1. Potassium chromoxalate, crystallised | 800 | 717 | 710—704 | 683 | 663 | 660—518 | 434 |
| 2. Potassium chromoxalate, saturated solution .. .. .. .. .. .. | 820 | 710 | 704—698 | 681 | 663 | 642—508 | 474 |
| 3. Chromium oxalate solution .. .. | 714 | — | 704—689 | — | 653 | 610—503 | 471 |
| 4. Chromium oxalate solution with an excess of oxalic acid .. .. .. | 800 | 710 | 704 \| 695 | 681 | 663 | 650—505 | 471 |
| 5. Red potassium chromoxalate solution | 800 | 710 | 704 \| 695 | 681 | 663 | 633—502 | 467 |
| 6. Ammonium ferric oxalate solution .. | 698. 623 | — | — | — | — | — | 489 |
| 7. Potassium manganic oxalate solution | 704 | — | — | — | — | — | 601 |
| 8. ,, cobaltic ,, ,, | 770. 710 | — | — | — | — | 657—543 | 469 |
| 9. ,, cupric ,, ,, | 639 | — | — | — | — | — | 411 |
| 10. ,, chrom-malonate ,, | — | 714 | 701 | 681 | 660 | 655—507 | 465 |
| Chromium hydroxide dissolved in aqueous solutions of the following acids:— | | | | | | | |
| 11. Malonic acid .. .. .. .. .. .. .. | 714 | — | 695—689 | — | — | 655. 623—503 | 464 |
| 12. Succinic ,, .. .. .. .. .. .. .. | 740 | 727—715 | 707 | 693 | 679—670 | 655. 644—537 | 498 |
| 13. Formic ,, .. .. .. .. .. .. .. | 800 | 721—714 | 704 | 689 | 674—666 | 650. 611—544 | 470 |
| 13*a*. Acetic ,, .. .. .. .. .. .. .. | 800 | 721—714 | 704 | 689 | 676—668 | 648—549 | 483 |
| 14. Propionic acid .. .. .. .. .. .. | 800 | 729—717 | 707 | 689 | 676—668 | 655. 641—544 | 494 |
| 15. Butyric ,, .. .. .. .. .. .. | 800 | 729—717 | 707 | 689 | 676—668 | 644—544 | 480 |
| 15*a*. Isobutyric ,, .. .. .. .. .. .. | 800 | 729—717 | 707 | 689 | 676—668 | 644—544 | 482 |
| 15*b*. Valerianic ,, .. .. .. .. .. .. | 800 | 730—718 | 707 | 692 | 677—669 | 650—517 | 484 |
| 16. Heptylic ,, .. .. .. .. .. .. | 800 | 732—719 | 708 | 695 | 681—674 | 650—544 | 480 |
| 17. Monochloracetic acid.. .. .. .. | 740. 710 | — | 698—686 | — | — | 655—504 | 480 |
| 18. Dichloracetic ,, .. .. .. .. .. | 740. 721 | — | 689—681 | — | — | 655—513 | 480 |
| 19. Trichloracetic ,, .. .. .. .. .. | 740. 714 | — | 701—674 | — | — | 655—509 | 480 |
| 20. Tribromacetic ,, .. .. .. .. .. | 770 | — | — | — | 676—668 | 653. 610—534 | 459 |
| 21. Glycollic ,, .. .. .. .. .. | 758 | 723—714 | 706—695 | — | — | 670. 644—507 | 473 |
| 22. Lactic ,, .. .. .. .. .. | 770 | 721 | 707 | — | 676—665 | 629—533 | 467 |
| 23. Trichlorlactic ,, .. .. .. .. .. | 721 | — | 710 | — | 674 | 655. 610—526 | 483 |
| 24. Phosphoric ,, .. .. .. .. .. | 740 | — | 698—686 | — | 670—650 | 639. 621 | 471 |
| 25. Malic ,, .. .. .. .. .. | 729 | — | 707—695 | — | — | 670. 644—498 | 480 |
| 26. Tartaric ,, .. .. .. .. .. | 800 | — | 707—695 | — | — | 668. 639. 501 | 475 |
| 27. Citric ,, .. .. .. .. .. | 736 | — | 707—698 | — | — | 660. 629. 504 | 467 |
| 28. Isethionic ,, .. .. .. .. .. | 717 | — | 695—668 | — | — | 653—506 | 480 |
| 29. Chromium chloride solution .. .. | 717 | — | 704—689 | — | — | 653. 619—550 | 472 |
| 30. Colloidal chromium chloride solution | 800—750 | — | 710—695 | — | — | 665. 621—544 | 480 |
| 31. Chromium hydroxide .. .. .. .. | 721 | — | 710—692 | — | — | 665—617—547 | 473 |
| 32. Perchromic acid .. .. .. .. .. | 740 | — | — | 689—674 | 653—639 | 613—544 | 448 |
| 33. Chloro-purpureo-chromium chloride, 10 c.m. thick .. .. .. .. .. | 695 | — | — | 674 | — | — | 585 |
| 34. Chloro-purpureo-chromium chloride, 2 c.m. thick .. .. .. .. .. | 717 | — | — | — | — | 545—474 | 415 |
| 35. Xantho-chromium chloride, 15 c.m. thick .. .. .. .. .. .. .. | 698 | — | — | 674 | — | — | 585—572 |
| 36. Xantho-chromium chloride, 2½ c.m. thick .. .. .. .. .. .. .. | 698 | — | — | — | — | 544—444 | 414 |
| 37. Rhodo-chromium chloride, 15 c.m. thick .. .. .. .. .. .. .. | 740—704 | — | — | 674 | 663 \| 660 \| 650 | — | 599 |
| 38. Rhodo-chromium chloride, 2½ c.m. thick .. .. .. .. .. .. .. | 800—704 | — | — | — | — | 546—473 | 413 |
| 39. Leuto-chromium nitrate 15 c.m. thick | 701 | — | 683 | 660 | 650 \| 631 | — | 599—536 |
| 40. Potassium chromi-cyanide, 15 c.m. thick .. .. .. .. .. .. .. | 710 | — | 545—542 | 531—525 | 520—518 | 507—505 | 476 |
| 41. Chloro-purpureo-cobalt chloride .. | 710 | — | — | — | — | 571—467 | 414 |

compounds an unique absorption-spectrum (40). Continuous absorption to 710; then four bands at 545—542, 531—525, 520—518, and 507—505 respectively, and continuous absorption from 476.

I am not acquainted with any other compound of chromium giving absorption bands analogous to these, and further, this salt does not give the broad absorption in the green part of the spectrum so typical of most other compounds of chromium.

*Potassium Cobalti-Cyanide*, $K_6Co_2(CN)_{12}$.—A concentrated aqueous solution of this salt was used. It gave no absorption bands, nor did it give the broad absorption in the green and blue part of the spectrum which is known to be so typical of the cobalt salts.

### *Conclusions.*

1. The absorption-spectra of the salts examined, having the general formula $M_6'Cr_26C_2O_4$, is the same when compared in solution, and also when compared in the solid state; but the absorption-spectrum in the solid state differs from the absorption-spectrum of the same salt in solution, the bands in the former case being nearer the less refrangible end.

2. Chromium oxalate has been obtained, analysed, and its absorption-spectrum recorded, which has been shown to differ from that given by the complex salts.

3. It has been shown that a solution of chromium oxalate with an excess of oxalic acid yields (*a*) the same absorption-spectrum as a solution of Croft's salt,—

$K_2Cr_2 4C_2O_4$,—(*b*) while with a larger amount of oxalic acid it yields an absorption-spectrum identical with that given by the salts $M_6'Cr_2 6C_2O_4$, and the conclusion has been drawn that analogous hydrogen compounds exist in solution.

4. The corresponding complex oxalates of iron, manganese, and cobalt do not yield analogous absorption-spectra.

5. A salt of malonic acid, analogous in composition to the corresponding oxalic acid compound, has been obtained. It has been analysed, and its composition is $K_6Cr_2 6C_3H_2O_4 + 6H_2O$. Its properties and absorption-spectrum are given.

6. The absorption-spectra given by the solution of chromium hydroxide in the various organic acids used have been noted and compared, and their relations to chromium hydroxide have been shown.

7. The absorption-spectra given by solution of chromium hydroxide in the fatty acids are similar in character, but the absorption bands are moved towards the less refrangible end in the case of the higher acids of the series.

8. The band 710—692 is represented in all the compounds of chromium examined,—except in potassium chromi-cyanide,—sometimes moved to the less, sometimes to the more refrangible end of the spectrum.

9. The broad absorption in the green—650 to 550 approximately—is represented in all the compounds of chromium. Sometimes it is moved towards the red end of the spectrum, as in the case of chromium hydroxide, dissolved in an excess of phosphoric acid; sometimes it is moved towards the blue end, as in the case of the salts of the chrom-ammonium bases; and in the case of potassium chromi-cyanide it appears as a series of bands.

10. It has been shown that the salts containing the group $[Cr_2 10NH_3]$ give an absorption band at 674.

In conclusion, my best thanks are due to Professor E. Wiedemann for the kind help he has given me, and also for placing at my disposal his specimens of the chrom-ammonium and other analogous salts.

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# A REVISION OF THE ATOMIC WEIGHT OF BARIUM.[*]

## First Paper: The Analysis of Baric Bromide.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 247).

### *The Properties of Baric Bromide.*

Baric bromide crystallises from aqueous or dilute alcoholic solutions in doubly terminated monoclinic[†] prisms, which are somewhat hygroscopic, but not deliquescent in ordinary weather.

The crystallised salt contains two molecules of water, together with the slight excess which is usually to be found in such crystals. Below the temperature of 70° in somewhat moist air, or at the ordinary temperature in perfectly dry air, it loses one of these molecules.[‡] The other one is retained until a temperature of from 100° to 130° is reached, according to the hygroscopic condition of the surrounding air.

The accuracy of the final result for the atomic weight of course depends upon the complete absence of water from the dried salt; hence an especial series of experiments was made to determine the conditions under which the water was completely expelled. Upon heating to redness, the salt is very slightly decomposed (Schultze, *Journ. Prakt. Chemie*, [2], xxxi., 407); hence in all cases where a high heat was used, the amount of baric hydroxide and baric carbonate formed were determined by means of very dilute standard hydrobromic acid, using phenolphthalein and methyl orange respectively as the indicators. The accuracy which it is possible to attain in this process was a great surprise. If a very small amount of pure boiled water is used for the solution of the baric bromide, a deficiency of less than a tenth of a m.grm. of bromine in 5 grms. of the salt is detected with the greatest ease. The correction applied to the weight of the baric bromide was of course always the calculated difference between the weights of the bromide and the hydroxyl, or the carbonic acid, which had taken its place. For example, a deficiency of 0·81 m.grm. of hydrobromic acid, found by alkalimetry, involved a correction of 0·63 m.grm. if the alkaline earth had been found in the form of hydroxide, or 0·50 m.grm. if it had been found in the form of carbonate. Since baric carbonate is very faintly alkaline to phenolphthalein, this correction is not absolutely exact; but its error is an infinitesimal one so far as this work is concerned. It is probable that, if any traces of oxide were formed, they were converted into hydroxide or carbonate before the crucible cooled.

One experiment showed that 1·6 grms. of baric bromide dried at 136° lost 0·4 m.grm. on being heated to dull redness. On another occasion, 3 grms. of baric bromide which had been dried at 200° to constant weight lost 0·50 m.grm. upon heating to dull redness. Alkalimetry indicated that 0·32 m.grm. should be added to the last weight as a correction for the bromine lost; hence the corrected loss was 0·00018 grm., or 0·006 per cent. A third trial gave the corrected loss of 3·5 grms. of baric bromide between 185°, and a dull red heat as 0·00027 grm., or 0·008 per cent. Again, 3·4 grms. of a less pure specimen of the salt lost 1·2 m.grm. between 200° and dull redness, of which loss eight-tenths of a m.grm. was accounted for by the baric carbonate found in the dissolved residue. In Experiment 19 about 3·5 grms. of the salt dried at 260° lost 0·04 m.grm. on heating to 340°, and 0·27 m.grm. more upon subjection to a red heat. In order to prove that the method of desiccation over sulphuric acid was sufficient for the purpose in hand, this specimen was again heated to 400°, and cooled in a vacuum over phosphoric oxide. After the admission of dry air the crucible and contents were found to have *gained* a little less than a twentieth of a m.grm. Since seventeen one-hundredths of a m.grm. must be added to the last weight of the salt to correct for the amount of alkali found, it is evident that the salt dried at 340° in the first place could not have retained more than 0·005 per cent of water, which could be expelled at a red heat.

The most severe test of the hygroscopic constancy of baric bromide was obtained by fusion. 17·4841 grms. of baric bromide, which had been thoroughly dried at a dull red heat, were fused in a platinum crucible, and were found to have lost 4·1 m.grms. during the process. 2·25 c.c. of twentieth normal hydrobromic acid were required to render the solution of the clear cake neutral to phenolphthalein, and 0·10 c.c. more made it strongly acid to methyl orange. These figures involve a correction of 7·0 m.grms. to the second weight of baric bromide, making it 17·4870 grms. The excess of this weight over the first (17·4841) is completely accounted for by the knowledge that a slight indeterminable correction (from 0·010 to 0·03 per cent) should have been applied to the earlier one, owing to its previous loss of bromine. The crucible was found to have lost 0·20 m.grm.

Again, 2½ grms. of baric bromide heated to constant weight at 185° lost 2·11 m.grms. on being fused in a double crucible. Of this weight all but 0·17 m.grm. (0·007 per cent) was accounted for by the amount of alkali found in the dissolved residue (Experiment 13). In

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[*] *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

[†] Werther (*Journ. Prakt. Chemie*, xci , 167); also Von Hauer (*Journ. Prakt. Chemie*, lxxx., 230). Rammelsberg states that the salt is isomorphous with baric chloride (*Pogg. Ann.*, lv., 237).

[‡] 2·8688 grms. of crystallised baric bromide lost 0·1547 grm. on heating to constant weight at 70°—80°; the residue lost 0·1533 grm. more upon heating to constant weight at 160°. Compare Graham Otto ("Michaelis," iii., 662). 2·0506 grms. of baric bromide, which had been powdered and dried over sulphuric acid to constant weight, lost 0·1181 grm. upon drying at 200°.

Experiment 4, given below, the bromide was also fused. Although this sample was not weighed at any lower temperature, it is evident from the amount of silver it required that about the same relation must hold true. It is a necessary conclusion from these results that baric bromide loses no more water upon fusion than upon being heated to dull redness without fusion. This constancy of hygroscopic condition gives strong ground for the inference that the ignited salt is wholly free from water, and that the salt dried at 180° contains only about seven-thousandths of one per cent of the impurity. Moreover, it is very unlikely that water and baric bromide could remain together at a red heat without mutual decomposition. The question of the absolutely anhydrous condition of most substances must necessarily be a matter of inference, because our methods for the determination of a few tenths of a m.grm. of water in the presence of a large amount of other material, which may be volatilised, are not sufficiently accurate to furnish direct evidence upon this point. Our knowledge regarding baric bromide is hence as full as it is possible to obtain.

The specific gravity of baric bromide has been determined by Schiff (*Liebig's Annalen*, cvii., 59; also cviii., 23). According to his results the crystallised salt is 3·69 times heavier than the same volume of water, while the anhydrous salt is 4·23 times heavier. Since it is important in reducing weights to the vacuum standard to know the exact values of these physical constants, new determinations were made. Carefully re-distilled dry toluol, in which baric bromide is insoluble, was taken as the liquid to be displaced, and two specific gravity bottles were used. The weight of water filling the first bottle was found upon three trials to be 11·4117, 11·4133, and 11·4120 grms., these values being corrected to 4° for the expansion of the water, but not corrected for the expansion of the glass (24°) nor for the air displaced by the water and weights. An approximate determination of the coefficient of expansion of toluol gave the means of reducing all the weighings with that liquid to the same standard of 24°. Three weighings gave results for the weight of toluol, filling the bottle, to be 9·8357, 9·8356, and 9·8342 grms.; and 4·4262 grms. of large clear crystals of baric bromide were found to displace 1·0141 and 1·0126 grms. of toluol at 24°. Hence the specific gravity of crystallised baric bromide at 24°, compared with water at 4°, is 3·852. No correction is made for the difference in volume of the weights employed.

A sample of baric bromide was dried at 200°, powdered very rapidly, transferred to the specific gravity bottle, and heated for a long time at the softening point of glass. After cooling in a desiccator, the weight of the baric salt was found to be 7·6808 grms. After filling with dry toluol, removing the atmospheric pressure, and shaking as usual, the gain in weight was 8·3878 grms., as a mean of two closely agreeing trials. Since the volume of the pycnometer had slightly altered during the heating, the bottle was remeasured and found to contain 11·3338 grms. of water at 4° (not corrected for the expansion of the glass), and 9·7685 grms. of toluol at 24°. These data give a result for the specific gravity of anhydrous baric bromide equal to 4·794.

Since the apparatus was not perfect, a new specific gravity bottle was prepared, which gave far more concordant results. With this apparatus 5·7271 grms. of baric bromide, dried for a long time at 200°, were found to displace the same volume as 1·1979 grm. of water at 4°. Here again the salt and toluol were at 24°, and the weights were not corrected for the different volumes of the brass. These figures indicate a specific gravity of 4·781,—not very different from the previous result, but very different from the value obtained by Schiff. The value 4·79 is used in all calculations which follow.

One hundred parts of water dissolve about 100 parts of anhydrous baric bromide at ordinary temperatures, and nearly 150 parts at the boiling-point of water.[*] The salt was found to be much less soluble in alcohol than one would expect from the literature on the subject.

A saturated solution in 87 per cent alcohol contains only about 6 per cent of baric bromide at the ordinary temperature. In absolute alcohol the salt is even less soluble. These facts had an important bearing on the methods of purification.

(To be continued.)

## RESEARCHES ON SAMARIUM.

By LECOQ DE BOISBAUDRAN.

Both absolutely and with relation to the orange of Sm the band $Z\zeta$ is strengthened if we take the reversed spark not at the edge but in the middle of the liquid. The quantity and the nature of the acid also modify the relative brightness of the two bands.

For the experiments summarised below I have employed samaria, tolerably pure, but not fractionated.

*Action of HCl.*—The aqueous solution of samarium chloride, approximately neutral, shows on reversal the band $Z\zeta$, very faint, and much inferior to the orange. On adding HCl to the liquid, the $Z\zeta$ is decidedly increased, and under favourable conditions it may even become as strong as the orange.

It is essential to have very clear solutions, and to use an earth which has been carefully cleansed, as the least impurities seem very injurious to the formation of $Z\zeta$.

*Action of $NHO_3$.*—With an aqueous solution of samarium nitrate, almost neutral, the band $Z\zeta$ is ordinarily much fainter than the orange. But if we add to the liquid a sufficiency of nitric acid, $Z\zeta$ becomes very decidedly stronger than the orange, at least in concentrated solutions. Without reaching such an intensity $Z\zeta$ is strengthened if we add nitric acid to a hydrochloric solution of Sm.

The band $Z\zeta$ has not the same aspect with HCl and with $NHO_3$. In HCl it is well defined on the right, but very vague towards the red. In $NHO_3$ the right margin is rather cloudy, and the left margin is merely a little more so than the right. The place of the right edge of the band with HCl is obscure with $NHO_3$, but the centre seems to be very little displaced. The dis-symmetry of the band in HCl renders the measurement of the centre difficult.

*Approximate Positions observed with Spectra of Mean Intensity.*

$Z\zeta$ in HCl, apparent middle .. .. $\lambda=614{\cdot}4$[*]
,, ,, right margin .. .. .. $\lambda=611{\cdot}8$[†]
$Z\zeta$ in $NHO_3$, apparent middle.. .. $\lambda=615{\cdot}5$
,, ,, right margin . .. .. $\lambda=614{\cdot}4$

*Action of Acetic Acid.*—With an aqueous solution of neutral samarium acetate $Z\zeta$ was not visible. On adding to the liquid from one-half to three-quarters of its volume of acetic acid, the fluorescence is slightly increased, but $Z\zeta$ did not appear. The addition of a noteworthy quantity of nitric acid caused $Z\zeta$ to appear, but it was still much fainter than the orange. On a large addition of nitric acid $Z\zeta$, however, becomes almost equal to the orange.

Samaria was dissolved in nitric acid in excess, and the solution was divided into two equal parts.

A certain volume of water having been added to A, the band $Z\zeta$ appeared very visible, though fainter than the orange.

A volume of acetic acid (8°, and sold as pure) equal to one-half the volume of the water put into A, was added to B. $Z\zeta$ was then visible, but much fainter than with A. There was then added as much acetic acid as had

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[*] See Graham Otto, *loc. cit.* Also recent experiments here.

[*] The intensity being greater to the right than the left, the real centre must lie a little more to the left.

[†] The position of the right margin is too much to the left.

been already introduced (in all the same quantity as the water put to A), $Z\zeta$ was weakened and became much fainter than it had been with A.

The acetic acid (or the impurities which it contains), appears therefore to prevent the production of the band $Z\zeta$.

*Comparison of $Z\beta$ and $Z\zeta$.*—I have mentioned the increase of these fluorescences, obtained by taking the spark from the middle of the liquid, and their decrease in presence of ferric chloride. $Z\alpha$ and Sm are, on the contrary, more or less enfeebled if the spark springs at the middle of the liquid, and are less sensitive to the action of ferric chloride.

In presence of an excess of HCl $Z\beta$ and $Z\zeta$ behave in an analogous manner, and are increased, especially $Z\beta$, whilst $Z\alpha$ is so to a less degree.

Nitric acid, on the contrary, causes $Z\beta$ and $Z\zeta$ to undergo very different variations, $Z\zeta$ being much augmented and $Z\beta$ much less.

*Comparison of $Z\alpha$ and $Z\beta$.*—An earth rich in $Z\alpha$ and $Z\beta$ was dissolved in HCl. It was evaporated to dryness and taken up in water. In this aqueous solution $Z\alpha$ was much stronger than $Z\beta$. On adding to the liquid half its volume of nitric acid $Z\alpha$ and $Z\beta$ were increased, $Z\alpha$ still remaining stronger than $Z\beta$. As much HCl was then added as there had been nitric acid previously introduced, $Z\alpha$ decreased a little (dilution of the solution ?), but $Z\beta$ was much strengthened, and surpassed $Z\alpha$.

A larger proportion of earth in the hydrochloric and nitric solutions seemed to favour $Z\beta$ compared with the orange of samarium.

We learn from the foregoing that the comparison of the reversal bands, $Z\zeta$ and orange, is somewhat delicate to effect in the various numbers of a fractionation.—*Comptes Rendus*, cxvi., p. 674.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending April 29th, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, May 15th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

By reason of the prevailing drought, the condition of the rivers throughout the month of April was exceptionally good, and the river-derived water supply was accordingly noticeable for the exceeding smallness of the proportion of organic matter present therein. Thus, calculated upon the amount of organic carbon found, the mean proportions of organic matter present in the different supplies may be taken as being approximately about one-tenth part of a grain per gallon in the case of the New River Company's water, and about one-seventh part of a grain per gallon in the case alike of the Lea-derived water furnished by the East London Company, and of the Thames-derived water furnished by the other five companies. As a result, moreover, of the excellent condition of the streams themselves, the difference in quality of the water supplied during the month, by the companies having a large, and by those having but a small storage area, was inappreciable. The degree of freedom from colour tint of the water, expressed in the case of the Thames-derived supply by the blue-brown ratio 20 : 11·5, as a mean, was, although high, not so high as has been noticed on other occasions of an exceptionally low reduction of the proportion of organic matter present in the water.

It is interesting to compare the results afforded by the water supply for April with those afforded by the supply for February, which was an exceptionally wet month, and with the average of those afforded by the supply for the first three months of the year, including of course February, as exhibited in the following abstract of results obtained with the Thames-derived supplies :—

| 1893. | Oxygen required for oxidation. Means. | Organic carbon per 100,000. Means. | Organic carbon per 100,000. Maxima. |
|---|---|---|---|
| February .. .. .. .. | 0·069 | 0·201 | 0·269 |
| First three months .. | 0·059 | 0·177 | 0·272 |
| April.. .. .. .. .. | 0·028 | 0·088 | 0·125 |

It will be noticed that during February, when the river was in a flooded state and the water supply in a less satisfactory condition than usual, the absolute excess of organic matter present in the supply for that month above the exceptionally small amount present in the supply for April was really very small, amounting in the case of the Thames-derived supplies taken for illustration, to not more than one-fifth part of a grain per gallon, that is, to less than the three-thousandth part of 1 per cent. It is further noticeable that while the mean ratio of nitrogen to carbon in the organic matter of the April supply was found to be as 29 : 100, the mean ratio in the organic matter of the February supply was only as 21·5 : 100, indicating the mainly vegetable origin of the excess of organic matter then present—and, indeed, it seems to be an invariable rule that when the quantity of organic matter present in the water is somewhat above the average, its mainly vegetable character is proportionally more decided.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 248).

### *Copper.*

The estimation of this metal is effected by precipitation as copper sulphide (CuS) by means of sulphuretted hydrogen or hyposulphate of soda, with subsequent conversion into copper oxide (CuO), either by ignition or dissolving and re-precipitating with caustic soda (NaHO). Ten grms. of the iron or steel are digested for a considerable time at a gentle heat, with 100 c.c. of nitro-hydrochloric acid, and the solution eventually carried down to dryness. To dissolve the dry residue add a small quan-

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* From *Industries*, April 4, 1893.

tity of hydrochloric acid, heat gently, and again take to dryness. Finally, re-moisten with a little hydrochloric acid, heat until solution is effected, dilute with hot water, and separate the silicon, &c., by filtration. The whole of the copper is contained in the filtrate, but before proceeding with the precipitation it is advisable to reduce the iron from the ferric, in which form it exists, to the ferrous state. This is accomplished by adding to the filtrate, made with water to a volume 250 c.c., an excess of sodium sulphite, and boiling until the sulphurous acid is expelled. To ascertain whether reduction is complete, a drop of the liquid is withdrawn at the end of a glass rod and brought in contact with a weak solution of sulphocyanide of potassium, when no red colouration should be found. The reduction of the iron is not absolutely necessary, as the same is effected by the sulphuretted hydrogen subsequently used for the precipitation of the copper, but by employing the sulphite the quantity of the sulphuretted hydrogen required is considerably lessened. Through the reduced solution pass a current of sulphuretted hydrogen until it is present in excess, allow to stand until the precipitated black copper sulphide ($CuS$) has completely settled, and pass the supernatant liquid through a Swedish filter-paper. Throw on the precipitate with the last portions, wash with water containing a little sulphuretted hydrogen, pierce the filter-paper, rinse the copper sulphide by means of a dilute solution of nitric acid into a beaker, some strong nitric acid being added, and the beaker and contents gently heated. When the whole, with perhaps the exception of a little free sulphur, has dissolved, the solution is diluted and filtered. The filtrate is then heated to boiling, a solution of caustic soda ($NaHO$) added, and the boiling continued. This results in the precipitation of the copper as copper oxide ($CuO$), which is collected on a filter, washed until free from alkali, ignited, contained in a porcelain crucible, and weighed. A hundred parts of copper oxide contains 79·85 parts of metallic copper.

A far more expeditious and less tedious method consists in precipitating the copper as $CuS$ by means of sodium hyposulphite, with subsequent conversion of the sulphide into oxide by ignition. The details of the method are as follows:—

In a beaker place 10 grms. of the sample, cover with 100 c.c. of dilute sulphuric acid (one part acid to three of water), and digest at a gentle heat. To the resulting solution add 6 c.c. of a strong solution of hyposulphite of soda, bring to boiling, with constant stirring, maintain at this temperature for twenty to thirty minutes, during which time the copper will be precipitated as black copper sulphide ($CuS$), and the solution, which, upon the addition of the "hypo" became milky, has regained its green colour. Collect the precipitate as rapidly as possible on a filter, wash a few times with water, pierce the bottom of the filter-paper, and rinse the contents into the vessel in which precipitation took place. Dissolve the copper sulphide in nitro hydrochloric, and evaporate the resulting solution, after the addition of about 10 c.c. of strong sulphuric acid, until heavy white fumes commence to appear; when diluted with water, heat to boiling, and add an excess of ammonia. Allow to stand in a warm place until any precipitate formed has completely settled; subsequently pass through a Swedish filter-paper, which, together with its contents, are well washed with water containing a little ammonia. Expel the excess of ammonia from the filtrate by boiling, and re-precipitate the copper as $CuS$, as before, by the addition of a little hyposulphide of soda solution. Filter, wash, ignite, and weigh the resulting copper oxide ($CuO$).

For the determination of very minute quantities of copper, dissolve 20 to 50 grms. of the metal in nitro-hydrochloric acid, evaporate nearly to dryness, digest the residue with an excess of ammonia, and compare the colour of a measured quantity of this ammonia solution with that of a standard solution of copper coloured with ammonia, or precipitate the Cu by any of the methods given.

### *Tungsten.*

The method of detecting and determining tungsten is comparatively easy, as upon treating the iron or steel containing the metal with nitrohydrochloric acid, with subsequent evaporation to dryness and resolution, the tungsten is converted into tungsten anhydride ($WO_3$), and the silica is coloured more or less yellow in proportion to the amount present.

For the determination a weighed portion of the metal is treated as in the estimation of silicon, with the exception that a lower temperature must be employed to effect solution, as also in the evaporation of the same, and the heating until the residue becomes black dispensed with, as this would render the $WO_3$ insoluble in ammonia and consequently vitiate the result. The filter containing the silica and tungsten anhydride, obtained as above, is pierced, and the contents rinsed, employing as small a quantity of water as possible, into a beaker covered with strong ammonia, and digested at a gentle heat for a considerable time. This results in the tungstic anhydride entering into solution as ammonium tungstate, while the silica is not attacked, and is separated by filtering, and, if desired, may be washed, ignited, &c. The filtrate, contained in a platinum dish, is evaporated to dryness, the residual ammonium tungstate heated to redness, whereby it loses water and ammonia, resulting in tungstic anhydride being formed, and upon cooling the dish, re-weighed to determine increase due to the $WO_3$ containing 79·31 per cent of tungsten. Tungsten is rarely or ever present in ordinary steels or irons. Alloys of iron and tungsten are readily formed, and tungsten steel is sometimes thus made.

### *Oxide of Iron.*

Although iron oxide is always contained in iron and steel, we are not aware of any simple and easy method, with the exception of the one now described, due to one of the authors, for its direct determination. The principle of Parry's method is that upon treating the metal containing oxide of iron with a mixture of potassium bichromate and sulphuric acid, the iron, &c., enters into solution, while the oxide of iron and silica remain unattacked. For the analysis, 10 grms. of the sample, contained in a beaker, are digested at a gentle heat (about 200° to 212° F.), with constant stirring, with 500 c.c. of a mixture of potassium bichromate and sulphuric acid—one part of the acid to six parts of a saturated solution of bichromate of potash.* When it is judged that the whole of the iron has dissolved, the solution is allowed to stand until the insoluble portions, oxide of iron and silica, have settled, when the supernatant is passed through a filter. The insoluble residue contained in the beaker is now washed three or four times with water by decantation, the washings being passed through the filter, and afterwards digested in a solution of caustic potash to remove the silica. Finally, the solution is diluted with water, passed on to the filter, the residue also being thrown on this time, the filter and contents washed three or four times with caustic potash solution, and thoroughly with water until all the alkali is eliminated. When this is effected it is removed to a crucible, ignited, and the residual oxide of iron weighed.

### *Titanium.*

The methods employed for the determination of titanium in iron and steel are far from satisfactory. The best results are obtained by Riley's method, the *modus operandi* of which is as follows:—Six grms. of the iron or steel, contained in a porcelain dish, are treated with 100 c.c. of nitro-hydrochloric acid, until dissolved, the solution evaporated to dryness, and heated strongly. On cooling

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* It has been proved experimentally that both oxides of iron are quite insoluble in this solution, and that the oxide exists in the metal as $Fe_3O_4$.

the dry residue is moistened with hydrochloric acid and the solution retaken to dryness. The dish and contents are again cooled, and sufficient hydrochloric acid added to cause, with the aid of heat, solution. When this is effected it is diluted and the silica, &c., filtered off; part of the titanium is contained in the filtrate and part remains with the silica. After thoroughly washing the filter and contents, remove to a platinum crucible, ignite, and when cool mix with six times its weight of bisulphate of potassium, and fuse. Reduce the cold fused mass to a powder and extract with cold water; the titanium enters into solution, while the silica is insoluble. Separate the silica by filtration, wash, and add the filtrate to the original acid solution of the metal. The next step is to reduce the iron of the mixed filtrates, containing the whole of the titanium, from the ferric to the ferrous condition, leaving only a *very small portion* in the former condition. This is effected by means of the addition of sodium sulphite, driving off the excess of sulphurous acid by boiling. The solution is now nearly neutralised with ammonia, ammonium acetate added, boiled, the resulting precipitate of titanic acid ($TiO_2$) and basic acetate of iron filtered off as rapidly as possible and dried. The mixed precipitate, contained in a platinum crucible, mixed with six times its weight of potassium sulphate fused, the mass reduced to a powder, dissolved in cold water, the solution nearly neutralised, boiled for some hours, and allowed to stand in a warm place. The precipitated titanic acid is then filtered off, washed with water containing a little sulphuric acid, ignited and weighed as rapidly as possible, it being slightly hygroscopic (100 parts of $TiO_2$ contain 60 of titanium). $Fe_2O_3$, even in very small quantities, considerably retards the precipitation of titanic acid; it is therefore expedient to add a little sodium sulphite to reduce the $Fe_2O_3$ contained in the solution previous to the final precipitation of the $TiO_2$.

A more satisfactory method, providing a large portion of the sample be operated upon—applicable, however, only to pig irons—is as follows:—20 grms. of the iron are digested with 150 c.c. of dilute hydrochloric acid, and when the metal is nearly dissolved, 100 c.c. of the strong acid added, and the solution boiled for some time. When it is judged that all the iron has dissolved, the solution is diluted, the insoluble portion—graphite, titanium, &c.—collected on a filter, washed with dilute acid water, a solution of potash to remove the silica, and finally with dilute acid and water to eliminate the alkali. The filter and contents are then transferred to a platinum crucible and the graphite burnt off at a bright red heat. The dirty brown residue, consisting of titanium, still contained in a platinum crucible, is fused with potassium bisulphate, extracted with water, and the titanic acid precipitated as before.

Titanium is found in small quantities in pig-iron, &c., but it does not appear to alloy readily with iron. Iron ores containing considerable proportions of titanium are difficultly smelted and costly to work. The resulting pig iron, although in most instances indicating only a small percentage of titanium, is, as a rule, unsuitable for the manufacture of Bessemer steel.

(To be continued).

**Detection of Nitrobenzol.**—J. Marpurgo (*Pharm. Post*).—The author places in a small porcelain capsule two drops of liquefied carbolic acid, three drops of water, and a fragment of potassium hydroxide the size of a pea. The mixture is carefully heated to ebullition, and the watery liquid to be examined is added. After prolonged boiling, a crimson ring appears on the margin of the liquid. If a saturated solution of chloride of lime is added, the ring becomes an emerald green. To detect nitrobenzol in soap, it is dissolved in water, mixed with an excess of milk of lime, extracted with ether, and tested as above.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, May 4th, 1893.*

Dr. ARMSTRONG, President, in the Chair.

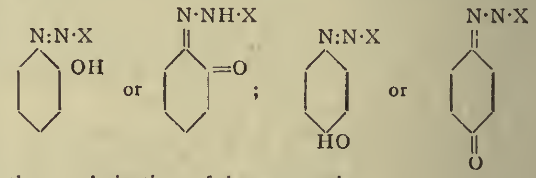
(Concluded from p. 251).

16. "*Notes on Capillary Separation of Substances in Solution.*" By LESTER REED.

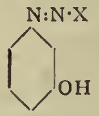
Although the separation of salts in solution by selective absorption in bibulous paper has been partly investigated by E. Fischer and E. Schmidmer (*Annalen*, cclxxii., 156—169), as I have, in ignorance of their experiments as well as of those of Schönbein, been recently investigating the same subject by a somewhat different method, I venture to briefly enumerate some of the observations I have made. My attention was first forcibly drawn to the subject by noticing the wide, colourless, very sharply defined margin which is obtained when a drop of moderately dilute solution of eosin (potassium eoside) is allowed to spread upon filter paper, although a saturated solution of eosin does not yield this margin. On adding potassium chromate to such a dilute solution of eosin, and repeating the experiment, the margin obtained is no longer colourless, but yellow, and the presence of chromate may be at once detected in this margin by touching it with a platinum wire moistened in a solution of silver nitrate, which produces a dark red spot on the yellow margin. If this yellow margin be cut off and extracted with water, a solution of potassium chromate free from eosin is at once obtained; and, conversely, eosin free from potassium chromate may be obtained if, after the drying of the drop, a drop of pure water be added and allowed to diffuse outwards from the centre; the appearance then obtained is that of a dark red central portion surrounded by a colourless margin, which is again surrounded by a yellow ring of potassium chromate, a practically complete separation or analysis of the mixture of the two salts being thus effected in a very short time. These, with a few other similar observations, are my initial facts, and naturally suggested the possibility of thus separating many other substances, as well as the use of porous media other than filter paper. I then observed that in some cases there was a very narrow colourless margin outside the yellow region of a drop of potassium chromate solution which had been allowed to spread on filter paper. At first I was inclined to suspect that this appearance was merely caused by the advancing solution crushing together and driving before it, by its expansion, some moisture already present in the filter paper. To prevent the drying of the drops during their expansion, I performed most of the experiments in an atmosphere saturated with aqueous vapour, by placing the filter paper, on which the drop lay on a small porcelain dish containing a little water, covering this with a bell jar moistened on the inside with water. When thus treated, a drop of moderately dilute solution of potassium chromate affords a most unmistakable colourless moist margin, in which silver nitrate fails to detect chromate. After this I examined in a similar way the diffusion of a mixed solution of ferric chloride and copper sulphate, testing the marginal region, after allowing about an hour for expansion, with potassium ferrocyanide, which demonstrated the existence of a marginal ring containing copper but free from iron. In the case of a solution of ammonia alum, using as tests for ammonium and aluminium respectively Nessler's test and tincture of logwood containing ammonium carbonate, no separation of the constituents was detected, both extending to the extreme limit of moisture; so that in this case I have not obtained any free water margin, and the same remark will apply to chrome alum. Employing a mixture of the solutions of copper sulphate, ferric chloride, and ammonia alum, a beautiful separation is readily effected. Externally in this case there is a ring of pure alum detectible by the logwood test, within which is an annular zone jointly occupied by copper sulphate and alum, which is shown to be free from iron by yielding a pure chocolate colour with potassium ferrocyanide; and, lastly, a central zone where all three salts are present, and which is coloured dark blue by ferrocyanide, the lines of demarcation between these three zones being perfectly sharp and definite. In applying the logwood test by means of platinum wire, it is necessary to dry the minute spots and to compare them with similarly dried spots yielded by the same test on clean filter paper. In the absence of alum, the drops are buff; in its presence, purple. Mercuric chloride is a salt which, even in saturated solution, very readily gives a free water margin. Caustic potash or potassium iodide may be used as tests for it. In a mixture of solutions of lead acetate and mercuric chloride, sufficiently dilute to give no precipitate, the lead is observed to outstrip the mercury. Platinum chloride very readily gives a margin, the test employed being reduction by heat; in the case of a strong solution, there is a tendency to form a double margin, which suggested to me the thought either that there might be two hydrates of platinum chloride present in solution, each possessed of a different diffusibility, or else that some of the lower chloride was present. As the width of the free water margin yielded in the course of an hour or so, in some cases at any rate, depends very much on the strength of the solution, I prepared a solution of ferric chloride of such strength as to yield no free water margin, and then diluted it until a slight margin began to appear. At this point I analysed the solution, which corresponded roughly to the ratio $FeCl_3 : 200H_2O$. On continuing the dilution in geometrical progression by continuously halving its strength, the free water margin rapidly increased in diameter, being always, however, separated from the iron region by a sharp line. When a dilution in the ratio of about $FeCl_3 : 30,000H_2O$ is reached, the iron seems to have almost lost its power of diffusing, getting little, if at all, beyond the space wetted by the drop when it first falls upon the paper. Of course, at this dilution it may be said that we are no longer dealing with ferric chloride, but with the products of its dissociation; and this explanation might be adequate but for the fact that an extremely dilute solution of sulphuric acid behaves in the same way. A drop of ferric chloride solution, while spreading upon filter paper, frequently presents an appearance, more or less noticeable, of concentric rings, suggesting, perhaps, the presence of more than one hydrate in solution. Imagining that the presence of hydrates in solution might be in some way or other connected with the formation or diameters of these free water margins, I prepared a solution of potassium bichromate corresponding in strength to Guthrie's cryohydrate, viz., $K_2Cr_2O_7 + 292H_2O$. It readily yielded a margin of water, and it is remarkable that this margin is of about the same width as that yielded either by a saturated, or by a very much more dilute, solution of the salt. I continued the dilution of this solution in geometrical progression, as with ferric chloride, until I brought it to 1/128th of the strength of the cryohydrate, but even this great dilution had little or no effect on the diameter of the free water margin, a result notably differing from that obtained in the case of ferric chloride or sulphuric acid. Copper sulphate solution, on the other hand, undergoes great change in diameter of free water margin on dilution. Hence it may be enquired whether a change in the diameter of free water margin, which must obviously represent a change in the relative velocities of water and the dissolved substance, may not in all cases be an evidence either of dissociation or of changes in the composition of the hydrates existing in solution. Sulphuric acid yields beautifully definite results, the test relied on being that of drying the filter paper at a high temperature, when the portion over which the acid has extended chars. A free water margin begins to be formed at about the strength of 1 part of acid by volume to 200 parts of water; and when a dilution of about 1 in 4000 is reached, the acid (as was the case with ferric chloride) seems to have almost totally lost its power of diffusing, and yields a relatively enormous free water margin. It would be very interesting if it could be shown that this inner zone of non-diffusible sulphuric acid represents a definite hydrate, the diffusibility of which is arrested by its enormous molecular weight, perhaps approaching those of such non-diffusible colloidal substances as the albumenoids; and such a hydrate might possibly be at or near the extreme limit of possible hydration of the acid. With regard to the employment of porous media other than filter paper, I have obtained satisfactory results, both with the mixture of potassic chromate and eosin, and with that of ferric chloride and copper sulphate, by using tubes containing powdered kaolin lightly rammed down, upon the top of which the solution was placed and allowed to soak downwards. I had hoped that this method of separation, or some modification of it, might have proved available for the separation of alkaloids from organic matters of different nature, with a view to their subsequent identification, but have hitherto been very partially successful in this direction.

17. "*Note on a Meta-azo-Compound.*" By R. Meldola and F. B. Burls.

While azo-compounds of the ortho- and para-series can be represented either as hydrazones or as true azo-compounds by the formulæ—



the azo-derivatives of the meta-series—



cannot be formulated as hydrazones. We have commenced a series of experiments having for their object the preparation of members of the meta-series, in order to institute a comparison between their properties and those of the ortho- and para-series. It is obvious that a comparative study such as we propose to undertake is calculated to throw light on the question of the constitution of organic colouring matters, as the "quinonoid" bonds are not present in the meta-compounds according to our present method of formulation. As the work must be for the present interrupted, owing to one of us (F. B. B.) having accepted an appointment away from London, we desire to place our results on record in this preliminary communication.

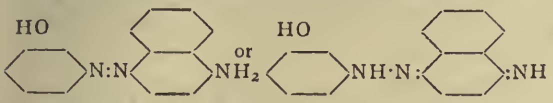
The first compound with which we experimented has not given a decisive result on account of certain practical difficulties which we have not yet succeeded in overcoming. The only satisfactory compounds which are worth studying from the present point of view are evidently those of the type—

$$C_6H_4{\cdot}OH{\cdot}N_2X\ [OH : N_2X = 1 : 3],$$

in which X is an *unsubstituted* hydrocarbon radicle. Metamidophenol was diazotised in presence of chlorhydric acid in the usual way and combined with α-naphthylamine, also dissolved in chlorhydric acid. The mixture of the two solutions gradually became of a deep violet-red colour. The azo-compound was finally precipitated by the addition of sodium acetate. The precipitate was collected, washed with water, and purified by dissolving it in cold dilute caustic soda, filtering and reprecipitating by acetic acid; it was then digested with dilute ammonia, washed with water, and crystallised alternately from dilute alcohol and benzene. Analysis showed that the substance was pure.

Calculated for $HO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$: C, 73·03; H, 4·94; N, 15·96.
Found: C, 73·10 and 73·14; H, 5·56 and 5·54; N, 15·94.

*Metaphenolazo α naphthylamine* may be fairly assumed to have the constitution expressed by the formula—



It crystallises in dull, orange-coloured needles fusing at 196°. Its solution in all solvents is orange coloured and it possesses strong tinctorial power as an orange dyestuff. It is both acid and basic in properties, readily dissolving in cold aqueous solutions of alkalis, forming orange-coloured liquids and also forming well defined salts with acids. The solutions of its salts are of a magnificent violet colour. If the hydrazone formula be assigned to the compound, it must be assumed that contact with acids causes its transformation into a compound of the azo-type, as the molecule is strongly basic towards acids and the presence of the amido-group is indicated by the readiness with which the compound can be diazotised. It dissolves in strong sulphuric acid, forming a dull magenta-red coloured solution, becoming violet on dilution, and on the further addition of water the sulphate separates out in bronzy crystals. Of the salts, the hydrochloride was specially examined. This was prepared by dissolving the base in boiling alcohol and adding strong chlorhydric acid; the colour of the solution changes from orange to violet; the hydrochloride separates out on cooling. The salt forms flat needles having a beautiful bronzy lustre. A specimen allowed to dry in the air for some time and then for a day in a vacuum gave the following results on analysis:—

Calculated for $HO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2,HCl,H_2O$: Cl, 11·18; N, 13·22; $H_2O$, 5·67.
Found: Cl, 11·36; N, 13·1; $H_2O$, 5·73.

The salt does not part with its water at temperatures below 110—120°, and the loss of the water molecule is accompanied by a change in colour from a metallic bronze to a dull green.

In order to further characterise the azo-compound, the acetyl derivative was prepared by boiling a solution of the substance in glacial acetic acid with acetic anhydride till the original violet colour of the solution had changed into orange. On precipitating with water and crystallising the product from dilute alcohol, it was discovered by analysis that it probably consisted of a mixture of a monacetyl with a diacetyl derivative; this was confirmed by the observation that the compound did not completely dissolve in dilute caustic soda, but left a slight residue. Purification was effected by this means, and the dissolved (phenolic) portion, having been precipitated by chlorhydric acid, was crystallised from dilute alcohol and then from dilute acetic acid till the melting point was constant. Beautiful golden scales were thus obtained melting at 232—235°, and giving on analysis results agreeing with the formula of the monacetyl derivative—

Calculated: C, 70·81; H, 4·91; N, 13·77.
Found: C, 70·53; H, 5·23; N, 13·70.

As this compound is phenolic, it is clear that the acetyl displaces amidic hydrogen, and, therefore, that the product has the formula $HO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_2H_3O$. It dissolves in alkali, forming an orange-coloured solution and possesses strong tinctorial properties. The non-phenolic derivative was not formed in sufficient quantity to enable us to obtain sufficient for complete examination. The melting point, after several crystallisations from dilute alcohol and benzene, was about 226°, and the nitrogen approximated in quantity to that required by the diacetyl derivative. The substance forms flat needles of a golden colour, and is also an orange colouring matter. As it is non-phenolic, the hydroxylic hydrogen is probably displaced as represented by the formula—

$$C_2H_3O{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_2H_3O.$$

The main object of the present investigation could not be realised in this case owing to the impossibility of displacing the $NH_2$ group by H. The method usually adopted in such cases was tried under various conditions, but the product was always a brown uncrystallisable resinous substance, which could not be purified by any artifice so as to give satisfactory results on analysis. The substance was phenolic and dissolved in alkali, forming a brown coloured liquid. It may have contained the naphthaleneazometaphenol sought for, but in its impure condition we could draw no conclusion with respect to its colour properties. The experiments are therefore being extended to other compounds of the same series.

18. "*The Influence of Moisture in Promoting Chemical Action.*" Preliminary Note. By H. Brereton Baker, M.A.

It has been shown by the author (*C. S. Trans.*, 1885; *Phil. Trans.*, 1888) that when moisture is removed as completely as possible, certain substances, *e.g.*, carbon, sulphur, phosphorus, &c., can be heated in an atmosphere of oxygen without undergoing visible combustion; and he has been engaged during the last two years in continuing the investigation, with the object of ascertaining in what way moisture promotes chemical action. One of the cases which he has studied is the formation of ammonium chloride from ammonia and hydrogen chloride. A difficulty presented itself at the outset in drying ammonia gas, as it is absorbed by phosphoric oxide; this was overcome by drying the gas as completely as possible by freshly ignited lime, after which it was found that phosphoric oxide did not absorb any appreciable quantity. Hydrogen chloride was dried in a similar way by sulphuric acid, and finally by a week's contact with phosphoric oxide. On allowing the dried gases to mix, *no ammonium chloride fumes were produced*, and no contraction was indicated by the mercury gauge attached to the apparatus; and it may therefore be concluded that ammonia and hydrogen chloride do not combine when dry. On introducing a small quantity of moist air, union at once takes place, however. In like manner, sulphur trioxide was found not to unite either with lime or barium monoxide or copper oxide. Furthermore, no brown fumes were produced on mixing dry nitric oxide with dry oxygen. The author is engaged in studying the effect of moisture on various types of chemical action, and he hopes soon to be able to communicate the results to the Society.

*19. "*The Genesis of New Derivatives of Camphor containing Halogens by the Action of Heat on Sulphonic Chlorides.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. J. Pope.

When the sulphonic chlorides described in a recent paper are heated at temperatures not very far above their melting-points, they undergo decomposition, sulphur dioxide being evolved. In the case of camphorsulphonic chloride, chlorocamphor is produced, in accordance with the equation $C_{10}H_{15}O{\cdot}SO_2Cl = C_{10}H_{15}OCl + SO_2$; at the same time a considerable quantity of an oil is formed, the nature of which remains to be determined. This chlorocamphor separates from cold dilute alcohol in arborescent forms; it melts at 137°—138°; analyses gave $C = 64·26$, $H = 8·47$, $Cl = 19·35$; $C_{10}H_{15}OCl$ requires $C = 64·37$, $H = 8·04$, $Cl = 19·09$.

By heating chlorocamphorsulphonic chloride, a well-defined dichlorocamphor is obtained, which crystallises from light petroleum in long prisms melting at 118° to 119°; like the sulphonic chloride from which it is derived it is dextrorotatory, its specific rotation in chloroform solution being a little higher than that of either of the known dichlorocamphors, namely, $[\alpha]_D = 85°$. Analyses gave $C = 54·27$, $H = 6·66$, $Cl = 31·84$ and $32·04$; $C_{10}H_{14}OCl_2$ requires $C = 54·34$, $H = 6·34$, $Cl = 31·99$.

The compound prepared from bromocamphorsulphonic chloride closely resembles dichlorocamphor, and crystallises from light petroleum in lustrous prisms melting at 142°—143°; like the latter, it has a high specific rotatory power, namely, $[\alpha]_D = 104°$, in chloroform solution.

These three derivatives of camphor appear to be different from any known compounds, and their further study will, it is hoped, throw light on the complex question of isomerism in the camphor series; it is possible that, starting from the corresponding sulphobromides, it will be possible to obtain new bromo-, dibromo-, and bromochlorocamphor derivatives, and in this way to establish fresh cases of isomerism; experiments with this object in view are in progress.

Dr. Armstrong informs us that Dr. Wynne and he have noticed in the course of their studies of naphthalene derivatives that a number of sulphochlorides undergo decomposition when heated above their melting-points, and that Dr. Wynne has observed that the sulphochlorides of some of the chlorinated toluenes behave similarly. The study of the behaviour of sulphochlorides and allied compounds generally when heated is therefore desirable, and will be carried on in the Central Institution laboratory.

## NOTICES OF BOOKS.

*Chemistry for All; or, Alternative Elementary Chemistry in Accordance with the Syllabus of the Department of Science and Art.* By W. Jerome Harrison, F.G.S., Chief Science Demonstrator for the Birmingham School Board, and R. J. Bailey, Assistant Science Demonstrator. London, Glasgow, Edinburgh, and Dublin: Blackie and Son, Limited, 1893. Small 8vo., pp. 150.

What "alternative elementary chemistry" may be might puzzle the "intelligent foreigner" of whom we have formerly read. If more treatises on elementary chemistry are needed, which we can scarcely admit, they might better be in accordance with the latest discoveries than with any "syllabus."

The work before us certainly contains no errors, but it is typically "departmental" and examinational. It is strange that the heads of the "department" never, when seeking for the causes of our difficulty in competing with Germany in the chemical arts, reflect that the course of instruction there given is not examinational.

*The Earth: Evolution of Life on its Surface, its Past, its Present, and its Future.* (La Terre, Evolution de la Vie a sa Surface, son Passé, son Présent, son Avenir). By Emmanuel Vauchez. In Two Volumes. Second Edition, 1893. 8vo., pp. 769. Paris: C. Reinwald and Co.

The author of the work before us is unquestionably an evolutionist and a Darwinian, in as far as he refers the origin and the development of species mainly to the "struggle for existence." He sets out with a general survey of our earth as a member of the group attendant upon the sun. He then proceeds to the origin of the solar system, the primitive fire-mist, the nebulæ observed in the heavens and photographed, and the successive birth of the planets. But whilst ably and eloquently describing the formation of nebulæ, suns, and planets, he says not a word on the genesis of the elements, as the material from which nebulæ, suns, and planets must ultimately have been derived. His views on this subject would have possessed a very high interest. Are the elements primordial, or have they been gradually evolved? He suggests, however, that in the præ-geological ages, at the time when the earth was a sun, the chemical elements themselves were dissociated. But had they ever been associated?

Life, and even thought, the author regards as a mere modification of *force*.

In discussing the origin and the development of life, M. Vauchez has the courage—still too rare in France—to reject the catastrophism of Cuvier. The account here given of microbia, of their signification, and of the part which they play, is fully on a level with the present results of research.

The remarks on the evolution of human civilisation, suggestive as they are, and humiliating as they must appear to modern "progressives," lie too far from the scope of the Chemical News for a critical analysis.

The different modifications of energy are here regarded as reducible to electricity.

An especial consideration is given in the first chapter of the third part to infection, to which no objection can be taken. But when M. Vauchez assigns an extinct anthropoid as the ancestor of mankind, and mentions an existing ape as making use of fire, we fear he is going beyond what has been demonstrated.

In the fourth part, treating of diet, the author considers that vegetarianism will in the future force itself upon mankind, and awaits from this change a physical and moral amelioration of our race! He does not seem to look forward to the synthetic production of food.

In the second volume the author goes back to consider gases, which, we submit, might have been more appropriately studied in an earlier part of the work.

The remainder of the author's studies fall entirely beyond our scope. Hypnotism, the history of religion, necromancy, metempsychosis, are subjects which we cannot discuss.

This work gives proof of extensive learning and of remarkable fertility and suggestiveness of thought; and to those able to use it aright it will prove valuable.

## CORRESPONDENCE.

### THE CHICAGO EXHIBITION.

*To the Editor of the Chemical News.*

Sir,—The New York Section of the American Chemical Society (Morris Loeb, Secretary, University of the City of New York, Washington Square, East, Room 16) will be happy to contribute, by all possible means, to the comfort and enjoyment of the foreign chemists who may visit New York on their way to or from Chicago during the World's Fair.

Visitors are requested to leave their names and addresses with the Secretary of the Reception Committee, who will also be glad to furnish all information at his command in reply to letters of inquiry.—I am, &c.,

(For the Reception Committee),
H. Carrington Bolton.

### OXIDATION PRODUCTS OF GLUCOSE.

*To the Editor of the Chemical News.*

Sir,—Mr. Langmuir consulted practical manuals about a question which has as yet no practical importance. As I happened to be in the library of Columbia College when I read, dated from that College, an inquiry as to the products of oxidation of glucose by Fehling's solution, I thought I would see whether this excellent library really lacked the desired information. An English translation of Strecker-Wislicenus mentions "tartronic and other acids" as the products. Beilstein gives full particulars. Both these books stand among the works of general reference, and it is therefore particularly easy for any one to consult them. But had the questioner traversed the few feet necessary to read the answer to his inquiry, he would have lost the satisfaction of knowing that, by the time he reads this, question and answer will together have travelled 12,000 miles.—I am, &c.,

A. E.

New York, May 15, 1893.

## OXIDATION PRODUCTS OF GLUCOSE.

*To the Editor of the Chemical News.*

Sir,—Most chemists will agree with your correspondent, Mr. A. C. Langmuir (Chem. News, lxvii., 204), that it is surprising that the products of the reaction of Fehling's solution on glucose should not have been more completely studied. In the absence of more exact information I may quote the following passage ("Commercial Organic Analysis," i., 225):—

"The action of reducing sugars on Fehling's solution is not precisely known, but among the products are:—1. Acetic and formic acids. 2. Certain non-volatile acids, especially tartrcnic, an acid forming uncrystallisable salts, and an acid decomposed with formation of humus-like products on heating its alkaline solution. 3. A gum-like substance."

I cannot now trace the source of this information, but believe it was derived from an abstract published in the *Journal of the Chemical Society* prior to 1882.

Of course it is well known, through the researches of Soxhlet and others, that the reaction between glucose and the alkaline cupric solution is far from constant, and that to ensure really accurate results a series of approximating experiments must be made.—I am, &c.,

Alfred H. Allen.

Sheffield, May 27, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 19, May 8, 1893.

**New Type of Phosphorites.**—Armand Gautier.—In these phosphates the aluminium salt preponderates. It is soluble in the cold in weak alkaline lyes, and to a large extent in ammoniacal ammonium citrate. Although the phosphoric acid is divided almost equally between the calcium and aluminium, these two phosphates are only associated or very feebly united.

**Remarks on the Specific Heat of Carbon.**—H. Le Chatelier.—The specific atomic heat of graphite (retort coke) increases from 250° to 1000° in a manner strictly proportional to the temperature. The coefficient of increase is much more considerable than it seems to result from the experiments of Weber.

**The Flames of Some Metals.**—Denys Cochin.—The compounds of the alkaline and alkaline-earthy metals, when volatilised in flames, yielded the first known spectra. These spectra in the visible portion are not identical with those obtained in making use of electricity as the source of heat. It seemed to me that it was interesting to examine how they terminated on the side of the most refrangible radiations, in a region where we have a great number of photographs of electric spectra, but no flame spectra. I have succeeded in photographing the spectra of coloured flames by the aid of a spectroscope of two quartz prisms of inverse rotations, with lenses of quartz and spar, according to M. Cornu's arrangement (*Journ. de Phys.*, vol. viii. (1879), p. 185). The frame of the dark chamber, which serves as an eye-piece, is slanting as in most spectrographs, and it is provided with a cylindrical bottom upon which steel springs apply exactly a flexible plate (Eastman's film). The sensitive preparation is then quite entire in its focal surface, which is a cylinder with a base nearly hyperbolic. The bottom of the frame has been brought to this form by approximations. The time for exposure is very long, half an hour to an hour. It is shorter if we use the flame of hydrogen as a source of heat. The results are approximately the same in each case. We always obtain the bands of the vapour of water $\lambda = 309$, &c., and we have never been able to obtain the metallic rays situate below at least without further prolonging the experiment. The rays are identified by comparison with those of an electric spectrum produced by means of the sparks of a Leyden jar, striking between the poles of cadmium, aluminium, &c., for about a minute. They are prevented from covering all the height of the flame spectrum by means of a small perforated screen, placed on the slit, which limits the spectrum for comparison to a small height. The following results were obtained:—

### *Alkaline Metals.*

*Lithium.*—$\lambda$ : 413.

*Sodium.*—Double ray $\lambda$ : 330·3 and 330·2, mentioned by MM. Kayser and Runge as obtained with the electric arc.

*Potassium.*—Rays $\lambda$ : 404 and 344·4.

*Rubidium.*—Visible ray $\lambda$ : 420, and besides, by employing the flame of hydrogen, two twin rays distinguished by Kayser and Runge as $\lambda : 359\cdot\frac{1}{356}\cdot7$ and $335\cdot\frac{1}{334}\cdot8$.

*Cæsium.*—Besides the visible blue rays $\lambda$ : 459·7·450, we obtain the invisible rays $\lambda$ : 388, $\lambda$ : 361·5, and $\lambda$ : 347·75.

### *Alkaline Earthy Metals.*

*Calcium.*—Visible ray $\lambda$ : 422·6. The exposure was prolonged with the flame of hydrogen for seventy-five minutes without obtaining the image of any invisible calcium ray, not even of the ray HH'. Nevertheless, the bands of watery vapour, $\lambda$ : 309, and three bands beyond them, likewise due to vapour of water, have been photographed.

*Strontium.*—Visible ray $\lambda$ : 460·7.

*Barium.*—Visible ray $\lambda$ : 487. Ultra-violet rays have not been obtained for any of these three metals.

*Thallium.*—Two invisible rays, situate respectively to the left of the rays 10 and 9 of cadmium at $\lambda$ : 353 and 378. The existence of these three rays in the flame spectrum approximates thallium to the alkaline metals.

**Attempt at a General Method of Chemical Synthesis.**—Raoul Pictet.—This paper will be inserted in full.

**Basicity and the Functions of Manganous Acid.**—G. Rousseau.—Under certain conditions manganous acid is capable of saturating 2 mols. of a diatomic base like calcium, but we cannot conclude that it presents the characters of a normal tetrabasic acid. The 2 mols. are not combined in the same manner. The first alone corresponds to two acid functions, the saturation of which produces stable salts of the type $CaO,MnO_2$. The second, which unites with $MnO_2$ only in strongly basic media, corresponds to two alcoholic functions. Hence we see that manganese dioxide should rank with the alcohol-acids, being in reality a bibasic acid with a complex function. The existence of the compound $2CaOMnO_2$, a derivative of the unknown hydrate $Mn(OH)_4$, establishes the tetravalence of manganese.

**Constitution of Licareol.**—Ph. Barbier.—This paper consists chiefly of diagrammatic formulæ.

**Syntheses with Aluminium Chloride.**—P. Genviesse.—In syntheses with aluminium chloride, we may obtain at once the formation of the normal and of an iso-compound. The production of the former is favoured by the use of a relatively small quantity of aluminium chloride.

**On a Liquid Isomer of Hydrocamphene.**—L. Bouveault.—The liquid in question, $C_{10}H_{18}$, is colourlees, having a faint scent of essential oil of orange, and boils at 148°—149°. Its vapour density leads to the molecular weight 138·2. Hydrocamphene, on the contrary, boils at 157°—158°.

**Chemical Composition of Oil of Niaouli.**—G. Bertrand. — The niaouli (*Melaluca vividiflora*) is a myrtaceous tree abounding in New Caledonia. Leaving secondary products out of the question, the author concludes that this essential oil (besides a dextrorotatory turpentine, $C_{10}H_{16}$), consists of a mixture of three bodies, eucalyptol, a carbide boiling at 175° (probably citrene), and a terpilenol.

**Systematic Glass-Moulding.**—Léon Appert.—The author's procedure requires to be described in detail. It can scarcely be placed under the heading "chimie industrielle" when the author himself informs us that the process is "purely mechanical."

### *Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 8.

This number contains no original matter.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Grinding and Polishing Quartz.**—I shall be much obliged if any of the readers of the CHEMICAL NEWS will refer me to some book where I can obtain instruction in grinding and polishing quartz plates and prisms. I am making some small pieces of apparatus of quartz, and should prefer to grind and polish them myself rather than get them done elsewhere. What I more particularly want to know is the material on which to grind, *e.g.*, iron, plate-glass, or stone, and the powders to use, whether emery, putty-powder, or rouge.—AMATEUR.

## MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Chemical Industry, 8. "The Movement of Air as Applied to Chemical Industries," by H. G. Watel. "New Cellulose Derivatives and their Industrial Applications," by C. F. Cross and E. J. Bevan.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 6th.—Royal Institution, 3. "The Waterloo Campaign," by E. L. S. Horsburgh, M.A.
WEDNESDAY, 7th.—Geological, 8.
THURSDAY, 8th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
—— Royal Institution, 3. "The Geographical Distribution of Birds," by R. Bowdler Sharpe, LL.D.
FRIDAY, 9th.—Royal Institution, 9. "The Recent Solar Eclipse," by Prof. T. E. Thorpe, D.Sc., F.R.S.
—— Physical, 9. "A New Photometer," by A. P. Trotter. "Notes on Photometry," by Prof. S. P. Thompson, F.R.S. "The Magnetic Field near a Wire," by Prof. G. M. Minchin, M.A.
—— Astronomical, 8.
SATURDAY, 10th.—Royal Institution, 3. "Falstaff": a Lyric Comedy by Boito and Verdi, by Dr. A. C. Mackenzie.

ERRATUM.—On page 253, col. 2, in the paragraph headed "Identity of Cystine and Ulexine," *cytisine*, the alkaloid of *Cytisus laburnum*, is erroneously printed "cystine," which is an entirely different substance.

## TO CORRESPONDENTS.

*B. Taylor.*—"Workshop Receipts," published by Spon.

*J. Clegg.*—After india-rubber has been vulcanised it cannot be dissolved off so as to be subsequently useful. You can dissolve the iron from the india-rubber by means of dilute sulphuric or hydrochloric acid.

*W. D.*—It is impossible to acquire a proper knowledge of chemistry without experimental practice in a laboratory. Any small room with a sink and a chimney in it can be used at first as a laboratory, and the necessary apparatus to begin with need only cost a trifle. Start with a small book on practical chemistry, and avoid theory at first. A useful book to begin with will be "Thorpe's Qualitative Chemical Analysis," published by Longmans, Green, and Co.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1750.

## ASSAY OF TIN ORE.

By THOMAS MOORE.

Having recently had occasion to make some enquiries into the different results obtained in the assays of tin ore, I was naturally led to look up and repeat some of the processes at present generally in use with a view of ascertaining wherein lay the sources of error, if any.

The first difficulty to be overcome is the satisfactory decomposition of the mineral. Some authors advise that the ore, *i.e.*, cassiterite, be treated with acid to extract as much soluble gangue as possible. At first sight this seems to be rather a risky proceeding, and accordingly the following experiments were instituted:—Five samples, each of 5 grms., were well boiled with aqua regia; three of them were then somewhat diluted with water and then filtered, the filtrate evaporated to dryness, and the residue, after fusion with dried sodic thiosulphate, dissolved in water and filtered. The filtrate was then acidulated with hydrochloric acid, and the precipitate so obtained boiled with strong hydrochloric acid to dissolve any stannic sulphide present. A piece of zinc was then added and allowed to dissolve completely in the cold, the solution again boiled to dissolve any metallic tin, and then tested with mercuric chloride and a solution of gold, neither of which gave any reaction. The remaining two samples were then evaporated to dryness, and the residue extracted with water. The solution treated as already indicated gave also no reaction for tin. It may therefore be safely assumed that the preliminary treatment with aqua regia does not cause any loss of tin; this is a point of considerable importance, as the presence of other elements only serves to complicate the remainder of the assay.

The method of fusion with dried sodic thiosulphate gives a complete decomposition if the mixture is kept fused for at least one hour; a shorter fusion than this gave in a few instances an undecomposed residue. The sulphide precipitate from the solution of the melt by hydrochloric acid is largely mixed with free sulphur, and exhibits a disagreeable tendency to creep over the edge of the filter and also to give a cloudy filtrate. The addition of ammonia acetate to the wash-water corrects this to a certain extent.

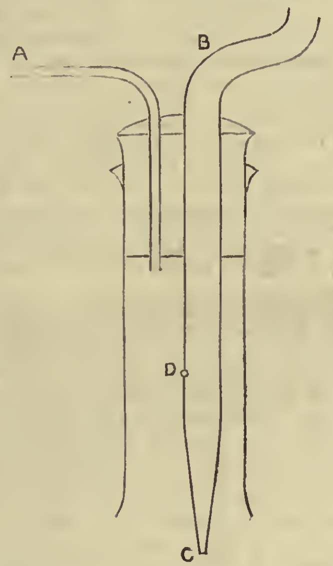
The method of Hallett was also tried. Four fusions were made, and in each case the solution was complete. The expulsion of the hydric fluoride is a serious drawback and occupies a considerable time.

The potassic cyanide proceeding has already been submitted to searching tests by Hofmann and others, so that there seemed nothing more to be done in connection with it.

The reduction of the mineral by zinc, as proposed by Wells, was then experimented with. This method consists in mixing the ore with zinc dust, and treating with hydrochloric acid, whereby the tin is reduced to the metallic state. This seemed to be a very feasible and ingenious way of attacking the problem, and, indeed, on trying the experiment it was found that the tin was rapidly reduced, and that on removing the reduced metal and repeating the treatment with the undecomposed residue, the reaction seemed to have been complete. Unfortunately, however, the sponge of tin, on being dissolved in hydrochloric acid, was found to contain enclosed ore particles, which settled to the bottom of the beaker glass as a heavy sediment.

The reduction was also tried by electricity by covering the mineral in a platinum basin with dilute sulphuric acid, inserting an electrode into the liquid, and connecting the basin to the pole of a galvanic battery, but with no better results; the sponge becomes inflated with the evolved hydrogen, and floats to the surface charged with particles of ore beyond the sphere of chemical action. Still the idea of reduction with metallic zinc seemed too good to abandon, and I therefore resolved to try its action in the dry way, and, after the inevitable failures, at last succeeded in the following manner:—

A porcelain crucible of from 10 to 15 c.c. capacity is taken, and a layer of zinc powder placed on the bottom of it; on this there is placed a mixture of 0·5 grm. of the ore with 5 or 6 grms. zinc powder, and over this another thin layer of the powder, and a solid well-burned piece of charcoal to keep a reducing atmosphere and to prevent the lid becoming cemented to the sides, and so giving rise to an explosion. The charged crucible is now placed in a red-hot muffle, and left there until the burning vapour of zinc has almost ceased; the crucible is then removed from the muffle, and allowed to cool without removing the lid. The combustion of the zinc vapour gives rise to the formation of a tube of oxide of zinc (presenting a very curious appearance), which, when dissolved in dilute acid, gives no trace of tin. The piece of charcoal is then removed, and the crucible and its contents treated with hydrochloric acid; after the first violent effervescence due to the excess of zinc is over, the sponge of tin is dissolved by boiling the liquid for a few minutes. The insoluble residue of silica, &c., will be found to be quite free from tin. The zinc powder used in this process must be quite free from lead, and is best prepared by triturating some melted zinc in a hot iron mortar, and separating the coarser particles with a fine sieve. The product so obtained is much coarser, but far purer, than the ordinary zinc dust.



Having obtained a solution of the ore, a variety of methods have been proposed for the estimation of the tin it contains. To precipitate the tin by metallic zinc, and weigh it as such, has never given good results in my hands, as the filtrate invariably contains notable quantities of the metal, even when the solution from which it was precipitated was but slightly acid; when the solution is rendered nearly neutral, then the filtrate is free from tin, but, on the other hand, the sponge is contaminated with either oxide or a basic salt of zinc.

Turning to the volumetric methods the choice seems to lie between the iodine process in alkaline solution or indirectly with an iron solution and potassic bichromate or permanganate in an acid liquid. Both procedures have yielded excellent results with pure materials, but with solutions containing, as they usually do, much zinc and free hydrochloric acid, the final reactions leave much to be desired. The utmost care must be taken to prevent access of air to the stannous solution, and, in diluting, only recently boiled distilled water is admissable. In this respect those processes involving the reduction of a ferric salt have this advantage, that the acid ferrous liquor may be exposed to the air for a comparatively long period without any appreciable difference. The direct titration of the stannous solution with potassic bichromate is not to be recommended, for, as first pointed out by Mohr, they are capable of existing together in the same liquid without decomposition.

Recognising these difficulties, and with the intention of devising a method whereby the solution of the reduced tin might be directly titrated, I attempted to apply the principle of the reduction of cupric to cuprous chloride by stannous chloride,—in fact, reversing the well-known process for the estimation of copper. It was soon apparent, however, that the eye could more readily distinguish the disappearance of the yellow tint than the first faint traces of its appearance, and, moreover, the presence of suspended matter in the liquid still more obscured the change. After a number of experiments the following course was at last adopted:—

Dissolve the sponge in hydrochloric acid in a flask through which a current of $CO_2$ circulates, add to the hot solution a known quantity of ferric chloride solution, allow to cool, and filter rapidly by suction; then titrate the excess of ferric chloride with cuprous chloride (Winckler's process) with KCyS as indicator, and from the amount of iron reduced the tin contents may be easily found.

The advantages gained by titration with cuprous chloride are, that the large excess of zinc chloride does not affect the reaction, neither does the presence of iron, which is, of course, already present as a ferrous salt. The flask in which the solution takes place is fitted with a doubly perforated cork containing two glass tubes. The tube A is connected to a $CO_2$ apparatus; B is of larger diameter, and is gradually drawn to a narrow tube at C. About an inch above this in the wide part a small orifice is blown (D); the object of this hole is for the escape of the $CO_2$, &c., so that when the ferric chloride is run into the solution by placing the tip of the pipette at D, the liquid clinging to the sides of the tube drops into the inside of the flask from the point C, thus avoiding being blown back in the tube, and at the same time preserving a non-oxidising atmosphere in the interior. Such an arrangement is exceedingly useful in the distillation of liquids, as in the Kjeldahl process, and effectually prevents any of the solution being carried over into the distillate.

Unfortunately, however, in the course of analysis tin is generally separated as the stannic sulphide, or at least in a stannic condition, in which state the volumetric methods are not available, so that if they are to have any technical value some rapid and simple process must be applied for the reduction of the stannic chloride, without, if possible, reducing the tin to the metallic state, and re-dissolving with all its incidental inconveniences. Boiling with metallic copper cannot be applied owing to the formation of cuprous chloride, which reduces the ferric chloride; metallic iron is also efficacious, but loads the solution with a ferrous salt, and the same applies to nickel and cobalt. Metallic lead, however, gives a perfect reduction without at the same time precipitating any tin. The solution should be concentrated to a small volume, and contain about one-fourth of its bulk of strong hydrochloric acid; 5 or 6 grms. of grain lead are then added, and the flask gently heated on the water-bath for a couple of hours, or raised nearly to the boiling-point for fifteen minutes. If too much hydrochloric acid is added, there will be a copious formation of chloride of lead crystals; this, however, does not interfere with the reduction. The liquid is now poured into an excess of ferric solution, and the residual lead and its chloride washed by decantation, after which it only remains to titrate the unreduced iron with cuprous chloride.

The results of a large number of trials with samples of known percentage were very satisfactory, and the time required for the assay need not exceed one hour—indeed, when everything is in readiness, not more than half that time is necessary.

Noumea, New Caledonia.

## ON THE ANALYSIS OF PIGMENTS WHEN GROUND IN OIL.

By J. B. HANNAY, F.R.S.E., F.I.C.

In preparing a pigment for analysis by separating the solid material from the oil in which it is ground, much trouble and loss of time sometimes occurs owing to the peculiar behaviour of the oil. With moderate quantities of most solvents the oil does not form a true solution, but a mixture standing midway between a solution and an emulsion, which so affects the contained solids that the mixture is extremely difficult to filter.

With solvents such as chloroform or bisulphide of carbon, which have a high density, it is very difficult to obtain a clear filtrate, and the separation of the oil is a tedious operation; but with fluids of lower density, such as benzene or ether, results may be obtained which leave nothing to be desired.

When entering upon the work it was necessary to clear a number of fallacies out of the way—and one especially, which had obtained a very firm hold on the literature of pigments. It has been long held that the oil in which the "Dutch" white-lead (basic carbonate) is ground forms some combination or "saponification" with the lead—forming, indeed, "lead soap." In a paper by Mr. Leighton and myself (*Proc. Chem. Soc.*, May 4, 1893), it has been clearly shown that in no case is there the slightest action between white-lead and oil, but that they simply mix mechanically as do all other pigments.

Were not this the case, the analysis of white-lead in oil would be a difficult and uncertain operation; but after devising tests which detect one part of oleate of lead in a million of pigment, it was shown that in no case is there found any oleate or similar compound due to the action of the oil.

The point in technical analysis which I am about to emphasise needs this preliminary explanation, as I find that the belief in saponification of oil by white-lead is not confined to ignorant tradesmen, but has been adopted by professional chemists. Lately, one chemist (Harland, *Journ. Soc. Arts*, xxiv., March, 1893) stated that he had examined hundreds of samples of white-lead, in all of which he found combination between the white-lead and the oil; and he has since affirmed (*Proc. Chem. Soc.*, May 18, 1893) that it is impossible to wholly remove the oil from an ordinary white-lead paint by means of ether.

How, then, does this chemist analyse his samples of white-lead, and does he report on the percentage of oleate of lead present? In contradiction of these statements, I assert that no oleate of lead or other lead compound is ever formed when white-lead is mixed with linseed oil, and that it *is* possible to absolutely free white-lead or any other pigment from oil by *many* solvents, but that this can be done with greatest ease and rapidity by using the method I am describing.

The peculiar property of the solution of oil to which I have referred may be entirely obviated by a very simple precaution. The emulsifying or structural property of the oil is entirely destroyed by the addition of a large volume of methylated ether, and instead of having an emulsified liquid difficult to filter, the pigment separates at once from the liquid, and settles to the bottom in flakes like a miniature snow-storm. The only points to be observed are, that the methylated ether must be fresh and contain its quota of methyl ethyl ether (as re-distilled ether tends to form the emulsion), and it must be added in very large excess—something approaching 100 c.c. to every grm. of the pigment. On shaking this up with the pigment, very rapid solution of the oil takes place, and the pigment settles at once free from any oil. The perfectly limpid solution of the oil is decanted, and successive small quantities of ether added to wash the precipitate free from the last traces of oil. This washing may, in the case of white-lead, be entirely conducted by decantation, as the lead pigment, owing to its great density, is *more easily* separated from the oil *than any other pigment.*

Even light flocculent pigments like oxide of zinc settle in a few seconds when fresh ether is used in such great excess, as it preserves great limpidness and allows of immediate settling. Some raw siennas and umbers are so fine that they take more time to settle, and may even require to be decanted through triple Swedish filter paper; but most pigments are obtained in such a flocculent condition that filtration is rapid and easy.

By using 100 c.c. of ether to every grm. of pigment the latter is *absolutely freed from oil*, and after three or four washings to clear it of mother-liquor, it may be transferred to a filter and weighed or dried in the flask after the last decantation. On dissolving the white-lead, or oxide of zinc, or other easily dissolved pigment, in cold dilute nitric acid after the above treatment, it will be found that a perfectly clear solution will be obtained, giving no trace of cloudiness, showing that no trace of oil or oleic acid adheres to the solid pigment.

On passing sulphuretted hydrogen through the etherial solution of the oil, no trace of colouration is produced, showing that no oleate of lead or other lead compound has gone into solution with the oil, so that an absolute separation has taken place, as this test will show one part of dissolved lead in a million of pigment.

On distilling off the ether and heating to drive out any traces of alcohol, the oil is obtained pure and may be weighed.

I have conducted hundreds of analyses in this way, but will only quote some typical results of experiments which were done to test the process. The mixtures, when excess of oil was added to the commercial paint, were made most intimately by long grinding in a mortar.

| Taken. | | Found. | |
|---|---|---|---|
| White-lead. | Oil. | White-lead. | Oil. |
| 88·48 | 11·52 | 88·51 | 11·56 |
| 91·75 | 8·25 | 91·64 | 8·37 |
| 93·50 | 6·50 | 93·46 | 6·51 |
| Zinc oxide. | Oil. | Zinc oxide. | Oil. |
| 81·73 | 18·27 | 81·75 | 18·18 |
| 77·44 | 22·56 | 77·62 | 22·60 |
| Ultramarine. | Oil. | Ultramarine. | Oil. |
| 73·79 | 26·21 | 73·74 | 26·25 |
| 78·22 | 21·78 | 78·23 | 21·80 |
| Raw sienna. | Oil. | Raw sienna. | Oil. |
| 83·21 | 16·79 | 83·25 | 16·74 |
| 79·43 | 20·57 | 79·43 | 20·62 |

**Results Obtained with Mixtures of Butters and of various Fatty Matters by the Use of the New Method for Detecting the Falsification of Butters.—Auguste Houzeau.**—The author observes the turbidity of melted and filtered samples. Those which are partially insoluble must be falsified. Those which are less turbid, like normal butters, may be pure.—*Compt. Rend.*, cxvi., No. 20.

# A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

## FIRST PAPER: THE ANALYSIS OF BARIC BROMIDE.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 258).

### *Preparation of Materials.*

*Baric Bromide.*—This substance was prepared in five distinct ways, with the intention of determining whether the salt is capable of being obtained in a perfectly typical state.

In the first place pure baric carbonate was prepared from pure baric nitrate. To make this latter substance the baric nitrate of commerce ("purissimum"), containing traces of strontium, calcium, potassium, and sodium, was re-crystallised seven times from boiling water by cooling. Baric nitrate is the most convenient starting point for the preparation of a typical barium salt, since its solubility rapidly diminishes with the temperature, and is so much less than that of the calcium and strontium salts. Even after the second re-crystallisation the alcoholic fractionally precipitated extract of a large amount of the mother liquor, which had been evaporated with excess of pure hydrochloric acid, showed no trace of calcium or strontium bands in the spectroscope. The pure salt, which had been re-crystallised seven times, was dissolved in a large platinum vessel in water which had been distilled in a platinum retort, and was treated with an excess of pure ammonia water which had also never come in contact with glass or porcelain. Into this perfectly clear solution was led a current of pure carbon dioxide, prepared by the action of pure sulphuric acid on sodic hydric carbonate. It was found impossible to free such carbonic acid from a trace of sodium, shown by conducting the gas into a lamp flame, as long as the sodic hydric carbonate was dry. After this last substance had been submerged under two inches of water, the gas evolved was easily obtained in a perfectly pure state by passing it through a sufficient number of washing bottles containing at first a weak solution of sodic hydric carbonate and finally pure water.

The pure baric carbonate was washed with hot distilled water until 25 c.c. of the wash water showed no trace of ammonia on the addition of Nessler's reagent. The last washing was with water which had been distilled in platinum. The snow-white preparation was dried and gently ignited over a spirit lamp in a platinum dish.

From this baric carbonate three different preparations of baric bromide were made, by dissolving it in two different samples of hydrobromic acid and varying other conditions. The first sample of acid was prepared from perfectly pure bromine. This had been made by the distillation of a mixture of potassic permanganate with a dilute solution of an excess of potassic bromide and pure sulphuric acid. Before being converted into hydrobromic acid the bromine was re-distilled after solution in potassic bromide and agitation with zincic oxide (Stas, *Mém. Acad. Belg.*, N. S., xliii., Part ii., p. 38). The bromine was in the first place poured into pure baric hydroxide, and, after the separation of the greater part of the baric bromate, was converted into hydrobromic acid by pure sulphuric acid. The baric hydroxide is easily freed from the usual trace of chlorine by five re-crystallisations from hot water; in this case the substance was crystallised nine times. The sulphuric acid had been re-distilled three times, the first and last portions being rejected.

The dilute hydrobromic acid, containing a small amount of free bromine set free by the remaining baric bromate, was distilled. The coloured first portion of the distillate was thrown away, and a portion of the second fraction was analysed to prove its purity. 1·82471 grms. (in

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* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

vacuum) of silver (*see* "Silver"), dissolved with all possible care in the purest nitric acid, yielded 3·17641 grms. (in vacuum) of argentic bromide upon precipitation with a slight excess of the acid. Hence the percentage of silver in the precipitate must have been 57·446, a result which is essentially identical with Stas's result, 57·445.

In this hydrobromic acid a portion of the pure baric carbonate was dissolved, and the solution was evaporated with a slight excess of baric carbonate to the point of crystallisation. The crystals were dried over the water bath and ignited at a dull red heat over a Berzelius lamp for half an hour. The filtered solution was allowed to stand until neutral to phenolphthalein, showing that all the small amount of baric hydroxide formed upon heating had been eliminated, and after filtration was evaporated. As before, the mother liquor was rejected; the crystals were washed twice with pure re-distilled alcohol and dried in the air. These crystals formed the first preparation, designated I.*a*, and served for the two preliminary analyses.

The second preparation of baric bromide was made from a similar specimen of baric carbonate by its solution in hydrobromic acid, prepared essentially in the manner described in the work upon the atomic weight of copper (*Proc. Amer. Acad. A. and S.*, xxv., p. 197). To test the purity of this acid 1·60376 grms. (in vacuum) of silver were dissolved and precipitated by a slight excess of the acid, yielding 2·79184 grms. (in vacuum) of argentic bromide. Hence the percentage of silver in the precipitate was 57·444 (according to Stas 57·445). The baric bromide made from this acid was re-crystallised, ignited at dull redness, dissolved, allowed to stand exposed to the air, filtered, crystallised, dehydrated, and fused at bright redness by means of an alcohol lamp. Finally, after solution, filtration, slight acidification with hydrobromic acid, and two successive crystallisations, the small amount of substance which remained was used for Analyses 3 and 4 (Preparation No. I.*b*). The salt contained in the last mother liquor was fused into an absolutely clear limpid liquid, dissolved, faintly acidified, filtered, and re-crystallised, the crystals being washed with alcohol, and finally analysed under the designation No. I.*c* (Analysis 5). It is needless to say that in all the concluding operations platinum vessels and the purest water alone were used.

The second general method used in the preparation of baric bromide was based upon the decomposition of baric bromate. This salt was obtained in a very pure state by repeated re-crystallisation of the bromate remaining from the first preparation of hydrobromic acid by the method described above. In the course of the re-crystallisation it was noted that the glittering hard crystals emit brilliant flashes of bluish light upon being rubbed between the surfaces of moistened glass apparatus. This phenomenon takes place when there is no conceivable trace of organic matter present, and may be noticed even in the daylight. The substance was gradually raised to a dull red heat by means of a Berzelius lamp, no emission of light being noticed during its decomposition. The resultant baric bromide was dissolved, filtered, crystallised twice, washed with alcohol, and dried. After fusion over the spirit lamp the substance was re-dissolved, filtered, acidified with hydrobromic acid, and finally crystallised twice from water. Each yield of crystals was washed four times with the purest alcohol. In the first mother liquor a notable trace of sodium was found by the usual spectroscopic treatment, but no trace of calcium or strontium. The purest crystals were divided by yet another crystallisation into three fractions, which we may call II.*a*, II.*b*, and II.*c*. The last was obtained by the evaporation of all the mother liquor decanted from the first two.

The third method used for the preparation of baric bromide adopted baric nitrate as its starting point. This salt, which had been re-crystallised ten times, was dissolved in hot water and treated with the calculated amount of the purest obtainable potassium hydrate in a platinum bottle. The resulting baric hydrate was re-crystallised ten times from hot water, without being removed from the bottle; but the spectroscope still showed noticeable traces of potassium upon the usual fractional treatment. The hydroxide was then precipitated three times successively from aqueous solution by means of pure alcohol, the precipitate being washed each time with alcohol, with the aid of the filter pump. Even the second mother liquor showed no trace of potassium to the most careful scrutiny.

The pure baric hydrate thus prepared was dissolved in pure water in the platinum bottle, boiled for some time to drive off the alcohol, transferred to a Bohemian flask, and saturated with pure bromine. This substance had been prepared as just described (see *ante*), with the additional treatment of solution in pure calcic bromide and several distillations. The mixture of baric bromide and bromate was evaporated, powdered, and gradually raised to fusion in a platinum vessel. The mass was grey before fusion and pale green afterwards. The greenish cake was dissolved in water, filtered, acidified, crystallised, dried, and fused; and then this same round of operations was again repeated. The last pure white cake of baric bromide was dissolved, the solution filtered, and after being very faintly acidified with hydrobromic acid, was again crystallised. The final crystals were washed four times with alcohol, and allowed to dry in the air. In the Table, which will appear later on, they are designated No. III. (Analyses 10, 11).

Since baric hydroxide is so easily re-crystallised it was hoped that a pure preparation might be obtained directly in this way from the baryta of commerce. It has been already said that five re-crystallisations remove the chlorine; five more remove the last traces of calcium. When, however, after seventeen re-crystallisations, the large amount of strontium present did not seem to be considerably diminished, this method was abandoned as a hopeless one.

A long series of qualitative and quantitative experiments upon the fractional precipitation of baric carbonate by the action of small amounts of carbon dioxide upon baryta water showed that this process also was utterly unfitted for the complete separation of strontium from barium, and accordingly this method was abandoned. The description and data of these experiments would require much room, and, since the work was not fruitful, they may well be omitted.

Because of all these unsatisfactory results, the baric hydrate was converted directly into baric bromide and bromate by the addition of pure bromine similar to that used in the preparation of Sample III. The large amount of bromide filtered off from the bromate was half crystallised out by boiling down the mother liquor in a platinum dish, treating with alcohol, and cooling. The mother liquor from these crystals contained most of the strontium. The solid was dissolved, boiled down, treated with alcohol, and cooled; and the new crystals were washed four times with alcohol. After repeating this round of operations once again, the mother liquor showed no trace of strontium.* The pure crystals yielded a faintly brownish mass upon fusion, and this in turn left a brownish precipitate upon solution. The clear filtered liquid was boiled down and treated with alcohol just as described above. The crystals were again fused, and again subjected to the same succession of operations. For the last time the crystals were raised to a dull red heat by means of a spirit lamp, and the residue was dissolved in the purest water in a platinum dish, allowed to stand exposed to the air until neutral, filtered, re-crystallised twice more, and washed with the purest alcohol. The resulting material was designated IV.*a* (Analyses 13, 14, 15). The last mother liquors were evaporated, and

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* This method of freeing baric from strontic bromide suggests P. E. Browning's work with amyl alcohol, published since the experiment recorded above was completed (*Am. Journ. Sci.*, [3], xliv., 459).

yielded IV.*b* (Analysis 12). Only about 15 grms. of such pure material were obtained from a kilogrm. of the baric hydroxide which served as the starting point. The earlier mother liquors containing strontium were used for the preparation of pure hydrobromic acid.

The fifth method for the preparation of baric bromide was the most complicated of all. A large amount of a solution of baric chloride ("purissimum") was allowed to stand for eighteen hours after the addition of a little pure baric hydrate and carbonate. To the filtered and slightly acidified liquid was added enough potassic chromate to precipitate about half the barium, the potassic chromate having been previously purified by continued shaking with a little baric chloride and hydrochloric acid, and by subsequent filtration. The large mass of baric chromate was washed by decantation with much water until no chlorine was to be found in the filtrate, and was almost wholly decomposed by strong nitric acid. The solution was diluted and shaken with the excess of baric chromate for a long time. Upon the neutralisation of the nitric acid in the clear yellow filtrate with pure sodic carbonate, the baric chromate was largely recovered, and after a thorough washing it was again dissolved in nitric acid, and the baric nitrate was repeatedly crystallised until it was wholly colourless and neutral. By means of gradually increasing heat, baric oxide was formed from this nitrate, the ignition taking place in a platinum crucible, and continuing until long after the frothing had ceased. The crucible itself lost several milligrms. during the process. The brownish residue was dissolved in water, and the clear colourless liquid was filtered from the brown precipitate. The baric hydroxide was neutralised with pure hydrobromic acid,* and the baric bromide was passed many times through the often repeated round of fusion, solution, filtration, and crystallisation, until the fused cake was perfectly clear and colourless. After being faintly acidified with hydrobromic acid, the pure salt was crystallised, washed, and dried as usual. This specimen, which had been growing smaller and smaller in amount during the manifold processes to which it had been subjected, was enough only for one analysis (No. 16) and was designated V.

Out of the baric bromate which remained from the fourth preparation two other specimens of baric bromide were prepared. The only point in which this preparation differed from the second method was the fact of the strong acidification of the bromide with hydrobromic acid just before the final series of crystallisations. The crystallisation was then continued until the mother-liquors proved to be absolutely neutral. The purest crystals were designated VI.*a*; the mother-liquor from them yielded VI.*b* (Analyses 17, 18, 19).

It seemed probable that if all these preparations gave about the same value for the molecular weight of baric bromide, they would fix this constant with comparative certainty. It is doubtful if the substance can be prepared in a state of absolute purity. Stas found it impossible to prepare any of his haloid salts in such a state (see Stas's "Untersuchungen," Aronstein, pp. 269, 279, 346), a small amount of silica always remaining. The attempt was made to eliminate the silica from the preparations described above by repeated ignition and fusion, and the exclusive use of platinum vessels; but it cannot be proved that the attempt was wholly successful. However, the salt was at least as pure as our usual standards of reference.

*Silver.*—Pure silver was prepared in the first place by the reduction of pure argentic chloride by pure milk sugar, after the well-known method recommended by Stas. A full description of the details is to be found in the account of the analysis of cupric bromide (*Proc. of the Amer. Acad. of Arts and Sciences*, xxv., 197, 198); indeed, some of the silver used in the present work was a portion of one of the large buttons made in 1890. Only in one particular was the mode of preparation modified: the silver was not heated with fused potassic hydroxide. Two or three buttons of the silver were fused with borax and sodic carbonate on hard-wood charcoal; this treatment made no essential change in its quantitative relations. The silver contained no oxygen, and gave very qualitative and quantitative evidence of purity (*Proc. of the Amer. Acad. of Arts and Sciences*, xxv., 197, 198; xxviii., 17, 28, 29).

All of the silver which has been thus far described was fused in the flame of ordinary illuminating gas. Since a strongly reducing flame was used, it was presumed that no silver sulphide was formed. Nevertheless, it was deemed advisable to prepare a sample of the metal which should be free from even the possibility of reproach. Ordinary hydrogen is apt to be quite as impure as illuminating gas, hence as little adapted for the present purpose. For this reason, pure hydrogen was made from pure hydrochloric acid by the action of zinc which was quite free from arsenic. The gas was driven through water, much potassic hydrate, through a tube containing beads moistened with argentic nitrate, and finally through potassic permanganate, into a gas-holder over water, where it remained for some time. It was burnt in an oxyhydrogen blowpipe provided with a complete platinum tip, and served for the fusion of the silver used in Experiment 19. For the support of the metal during its fusion a cupel of sugar charcoal had been made from pure sugar by the sole use of an alcohol lamp as the source of heat. The silver itself was made from the pure silver first described by dissolving it in nitric acid and electrolytically depositing it with the aid of two Bunsen cells (J. L. Hoskyns Abrahall, *Journ. Chem. Soc. Proc.*, 1892, p. 660), two plate of the same metal serving as electrodes. This method for the preparation of pure silver is a very satisfactory one. Since the silver was allowed to cool in an atmosphere of hydrogen, it could have contained no oxygen. The agreement of Experiment 19 with the others is satisfactory proof that the amount of sulphur contained in the first samples of silver must have been infinitesimal, if appreciable at all.

*Other Materials.*—The methods used for the preparation of pure water, pure nitric and sulphuric acids, and pure sodic carbonate, have been discussed at length in a previous paper (*Proc. of the Amer. Acad. of Arts and Sciences*, xxvi., 245—249). Precautions taken with regard to carbon dioxide, hydrobromic acid, and many other substances, are to be found under earlier heads. Alcohol was purified for the present investigation by repeated distillation in apparatus wholly free from cork or rubber connections. In some cases a platinum still was used.

The large mass of platinum used in the first experiments was kindly loaned by Professor Cooke, but subsequently a quantity was purchased especially for the work. The methods used in freeing the surface of these vessels from iron are described in the fourth paper upon the revision of the atomic weight of copper (*Proc. of the Amer. Acad. of Arts and Sciences*, xxvi., 249).

(To be continued.)

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## PROGRESS OF CHEMISTRY AS DEPICTED IN APPARATUS AND LABORATORIES.*

By H. CARRINGTON BOLTON.

From the very earliest times many arts were practised involving chemical operations, such as working in metals, purification of natural salts for pharmacy, &c., dyeing of cloths and the preparation of pigments, brewing of fermented liquors, &c.; hence we find that long before chemistry became a science, even before it became inocu-

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* This acid was from the same sample as that employed in making specimens I.*b* and I.*c*.

* (Abstract). From the *Transactions of the New York Academy of Sciences*, Vol. XII.

lated with the virus of alchemy, furnaces and apparatus of earthenware, metal, and glass, adapted to special work, were in common use.

The important adjuncts to laboratory utensils for the mechanical operations of pulverising, grinding, sifting, &c., and the use of scales in a general way, date from the very beginnings of human industry; these we disregard in the main and confine our study to apparatus more strictly adapted to chemical operations.

In tracing the progress of chemistry by reviewing the forms and variety of apparatus used at different periods, we do not attempt to establish definitely the date of introduction of a given instrument except in a few instances to be noted in their places. To assign dates to the origin of apparatus that was universally employed before being specifically described is obviously impossible, especially since we shall depend upon drawings to illustrate the subject, and these drawings are commonly far more recent than the apparatus portrayed.

The Egyptians attained great skill in industrial arts at a remote period, and have left records of a most enduring character, pictures cut in their granite tombs and temples. There we see the processes of gold-washing and smelting; the use of blowpipes and of double bellows for intensifying heat, various forms of furnaces, and crucibles having a shape quite similar to those used to-day. Some of these crucibles preserved in the Berlin Museum date from the Fifteenth Century B.C.

Glass-blowing is a mechanical operation, but the preparation of the glass itself is a chemical process. The skill of the Egyptians in manufacturing glass is depicted on monuments of Thebes and Beni Hassan, and dates at least as far back as 2500 B.C.

Syphons for decanting wine, and on a large scale for draining land, were in use in the fifteenth century B.C. (Wilkinson).

The earliest chemical laboratories of which we have any knowledge are those that were connected with the Egyptian temples. Each temple had its library and its laboratory commonly situated in a definite part of the huge structure; at Edfoo the laboratory leads out of the Prosecus-halls. In these laboratories the priests prepared the incense, oils, and other substances used in the temple services, and on the granite walls were carved the recipes and processes; these are still to be seen by the archæologist.

The Israelites driven out of Egypt carried with them to the promised land knowledge of the technical and artistic skill of their contemporaries, and the Holy Bible contains frequent allusions to industrial arts. Cupellation is plainly described by Jeremiah, metallurgical operations by Job, Ezekiel, and others, and bellows by Jeremiah. This subject, however, I discussed in a paper read to the Academy April 12, 1892.

Geber, the Arabian physician and chemist of the Eighth Century, wrote very plainly of chemical processes, describing minutely solution, filtration, crystallisation, fusion, sublimation, distillation, cupellation, and various kinds of furnaces and apparatus employed in these operations. Geber's works first appeared in a Latin translation from the Arabic at Strassburg, 1529; since then many editions in modern languages have appeared, but the drawings in all these I have seen are obviously of comparatively recent date.

Geber describes in detail the aludel (or sublimatory of glass), the decensory, apparatus for filtration, and the water bath. This latter instrument, however, is said to have a more remote origin, having been invented by an alchemist named Mary, who is identified with Miriam the sister of Moses; and the French name *bain-marie* is advanced as proof of this claim.

Perhaps the earliest drawings of strictly chemical apparatus are those in the so-called manuscript of St. Mark, which is a Greek papyrus on the "sacred art," preserved in Venice and recently edited by Berthelot. This embraces among other treatises the *Chrysopoeia of Cleopatra*, which dates from the beginning of the Eleventh Century. It contains, besides magical symbols, figures of distilling apparatus, the chief being an alembic with two beaks, resting on a furnace.

In manuscript No. 2327 of the Bibliothèque Nationale, Paris, which bears the date 1478, are interesting drawings of furnaces, alembics, matrasses, receivers, &c., of glass, earthenware, and metal. Some of them are copied from the manuscript of St. Mark. Professor Maspero, the Egyptian explorer, reports the discovery by natives of the subterranean laboratory of an alchemist of the Sixth or Seventh Century, at a point not far from Siout. This concealed laboratory contained a bronze furnace, the bronze door of another larger furnace, about fifty vases of bronze provided with beaks, some conical vessels resembling modern sand-baths, vases of alabaster, and gold foil of a low grade valued at over 350 dollars. In a corner of the dark chamber lay a heap of black fatty earth that the workmen seized upon and carried off, saying they would use it to transmute copper; "whiten" was their expression, but they evidenced a belief that this material was the "powder of projection" capable of changing copper to silver. This was in 1885. The substance on examination proved to be impregnated with some compound of arsenic, which would, of course, "whiten" copper.

The balance as an instrument of precision reached a high development under the Arabians as early as the Twelfth Century. The "Book of the Balance of Wisdom," written in the year 515 of the Hegira (1121—1122 A.D.) by al-Khazini describes minutely a water balance of great ingenuity, and the specific gravity determinations of solids and liquids made by its aid are marvellously accurate. The author also describes a specific gravity flask of a practical make which he calls the "conical instrument of Abu-r-Raihan." This treatise, with its illustrations of the balances and the flask, I analysed in a paper read to the Academy in 1876. (*Am. Chem.*, May, 1876).

In an interior view of a laboratory of the Fifteenth Century, by Vriese, very sumptuous appointments are seen; a lofty room with tiled floor, furnaces on the right under an overhanging hood, an altar on the left before which the alchemist prays on his knees, in the centre a table covered with apparatus, books, and musical instruments, in the foreground an alembic, overhead a lamp swinging from a ceiled roof. The whole indicates wealth and luxury contrasting strongly with later pictures of the laboratories of impoverished alchemists.

The interior of workshops of alchemists of the Sixteenth Century have been artistically painted by the celebrated Flemish artist David Teniers. Of these interiors I am acquainted with six different styles, having, however, many features in common.

The alchemists, influenced by the atmosphere of mystical associations prevailing in astrology and the black art, affected fanciful names for pieces of apparatus bearing accidental resemblance to objects in nature; the body of an alembic was a "cucurbit" or gourd; an alembic-head without a beak was a "blind alembic"; if the beak was joined to the body so as to make a circulatory apparatus, it was a "pelican," owing to its outline resemblance to this bird; two alembics joined by beaks were "twins"; a flask with a very long neck was a "bolt-head"; a flask with its neck closed before the blowpipe was a "philosophic egg." Again the cucurbit surmounted by the alembic-head was symbolically called "homo galeatus," a man wearing a helmet.

(To be continued).

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**Use of Superphosphates.** — Jules Joffre. — The author's experiments seem to show the possibility of the compounds of phosphoric acid soluble in water contained in manures being directly absorbed and assimilated by plants.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 9.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Extra Meeting, May 5th, 1893.*

Dr. Armstrong, President, in the Chair.

### *Hofmann Memorial Addresses.*

The President, in opening the proceedings, said they were met to do honour to the memory of a man to whom chemists throughout the world, and especially British chemists, are very deeply indebted—probably to a far greater extent than we shall ever be able to realise; a man who on account of his marvellous and manifold gifts will undoubtedly rank among the chemists of the Victorian era as second only to his great master Liebig. Hofmann, even if judged by his published work alone, would take the very highest position; but those who had known the man, however slightly, were aware that he was possessed of rare personal gifts which enabled him to exercise an influence extending far beyond the limits to which any purely scientific worker can attain. It is on this account very difficult to secure a satisfactory presentment of the man and especially of the influence which he directly and indirectly exercised on the development of chemical science and its industrial application. They, however, were fortunate in that they had succeeded in inducing several of the Fellows to co-operate in this arduous task, and although they could not hope to do all that is necessary, the contribution the Society was thus able to make will be exceptionally valuable, as the three gentlemen who would speak of Hofmann that night all had peculiar qualifications.

Lord Playfair, in days long ago, dwelt happily in the verdant and fertile fields of science, and the more often we had evidence of his perennial and vigorous youthfulness the more we must lament that he was ever led away into the tortuous paths of politics; in those almost prehistoric times he was not a mere spectator but an active worker, his name being associated in the records of science with those of the giants Bunsen and Joule. Among others there was a paper by him on "Transformations Produced by Catalytic Bodies," published forty-five years ago in the Society's memoirs, which was worthy of perusal even now, and which, he ventured to think, displayed greater philosophic grasp of the problem than the more recent essays on the subject. He had been astonished in reading through the early minutes of the Society to see how active an interest the then Dr. Lyon Playfair took in their work: how he was always proposing that something new should be done, and how very frequently his proposals were carried into effect. No one was so well qualified as Lord Playfair to picture to us the state of affairs chemical at the time of Hofmann's arrival here.

Sir Frederick Abel's qualifications were of a different order—he would speak directly of the man and of the conditions under which he worked at an especially interesting period in his career. He believed that Sir F. Abel's name was first on the list of Hofmann's first set of students, and that he was his first English assistant; he soon became and ever afterwards remained, he might say, his willing slave as well as friend, for Hofmann *had* the power—and hence his marvellous influence —of enslaving all who came under him, and of making them, whether they willed it or no, do the best work they were capable of. Sir Frederick Abel by virtue of his opportunities and his abilities was the man to whom alone we could look on the present occasion. His devotion to the Society was well known to most of the Fellows; but there were few besides the officers who have been concerned with him in the management of its affairs who are fully aware of the extent to which he had served the Society. His presence there to-night was in itself sufficient evidence of the deep interest he still took in their work and of his willingness to sacrifice himself; as all knew, at the present time, he was engaged in the conduct of an enterprise of extreme difficulty and magnitude—more than sufficient to tax the powers of the majority of men, but which appeared in no way to satisfy his insatiable greed of work.

Of Dr. Perkin, who would speak of the outcome of a part of Hofmann's scientific work, it was needless to say much. He was a man of whom it could truly be said that his works are the measure of his worth. If the walls of the room in which they were assembled could speak, it would be of his labours before all others that they would have to tell. The story that he had to relate was of entrancing interest—a true tale of magic, but full of deepest moral.

Lord Playfair said that, although, when he was at Giessen, Hofmann was about two years his senior in age, Hofmann was studying mathematics and physics, and although he mixed with the active workers in Liebig's laboratory, he was not one of the body, and did not begin to work there until some time afterwards; it was originally intended that he should devote himself to philology and law, of which he was during some time a student. Referring to his remarkable linguistic powers, he said he had heard him make speeches in several languages, and especially remembered one occasion when, in 1867, at a memorable banquet given by the French chemists to those of foreign countries, Hofmann proposed the health of their hosts in a capital French speech.

He then spoke of the position of chemistry in England prior to Hofmann's arrival. Both in the last and the early part of the present century, England was not wanting in great chemical investigators. Among others, Lord Playfair referred to Dalton, incidentally mentioning that he could never forget seeing his venerable figure, supported on the arm of Dr. Joule, come daily to hear him lecture at Manchester on organic chemistry. Except Graham, under whom the speaker studied in Glasgow in 1835—36, following him to London as private laboratory assistant, no one, however, had thought of opening his laboratory to students. Graham's example, however, spread, and several colleges, and even the universities, slowly adopted the view that laboratories were necessary to teach and train the chemists of the future; but all who desired to study organic chemistry flocked to Giessen, and returning from there acted as missionaries in spreading a knowledge of the new organic chemistry. An extraordinary influence was exercised by the publication, in 1840, of Liebig's celebrated work, "Chemistry of Agriculture and Physiology," which was heightened by a triumphal tour, made two years later, by Liebig, through this country, in which he was personally conducted by the speaker. The immediate effect of Liebig's tour was to make chemistry a popular science, and to induce colleges to open laboratories, and hence it was that the Royal College of Chemistry was founded in 1845. Two wise men were mainly instrumental in its establishment—the Prince Consort and the Queen's physician, Sir James Clark. They saw that all the chemical laboratories in existence in this country were mere accessories or subordinate to professional training, the students entering them rarely wishing to become chemists; and they desired to found a college where chemistry might be studied for its own sake. A college of this kind without endowments could not have been created without a strong popular feeling had arisen, such as Liebig's work had promoted.

After referring to Hofmann's appointment, his remarkable lucidity, and his marvellous powers of exciting enthusiasm, Lord Playfair spoke of the early success of the College of Chemistry, and then proceeded to explain how it was that it so soon ceased to exist as an independent institution. Every landowner had thought that Liebig's book was to be his salvation, and when it was found not to produce the expected results, popular belief in chemistry declined, and the support accorded to the college gradually dwindled. At this time the speaker resigned his professorship at the School of Mines, and Hofmann succeeded him, carrying with him the College of Chemistry, which then ceased to be an independent institution: the change was inevitable under the circumstances, but it was not good either for the college or chemical science. No doubt Hofmann felt this, and was affected by it when he was offered a professorship in the Berlin University, where he went in 1864.

Lord Playfair concluded his address by expressing the hope that he might live to see a new college or institute arise like a phœnix from the ashes of the old one, perhaps in connection with higher university teaching in London, as a supplement to, and not in competition with, existing laboratories, in which chemistry might be taught as an independent subject.

Sir **Frederick Abel**, at the outset of his address, referred to the commencement of his own career as a chemist as an illustration of the difficulties attending the attempts of young beginners with limited resources to acquire a knowledge of practical and analytical chemistry, with a view of adopting the science as a profession, half a century ago. In the autumn of 1844, he had entered the laboratory of the Royal Polytechnic Institution, only to find that the sole means of acquiring some practical knowledge consisted in plodding unaided through Brande's Manual, endeavouring to acquire experimental skill by preparing the elements and their compounds according to the directions therein given, and to become acquainted with analysis by following Andrew Parnell's tables. Several other young chemists, who afterwards became prominent pupils of Hofmann, were in a similar position at that time, and so, when the temporary laboratories of the new college were opened in the autumn of 1845, there was a small band of aspirants impatiently waiting to avail themselves of the benefits of the system of instruction which had already acquired so high a reputation on the Continent.

Sir Frederick then recited the history of the efforts made in this country as early as 1843 to establish an institution where the systematic study of chemistry as a profession in itself could be pursued, referring to the prominent part taken in the matter by Dr. John Gardner, the translator of Liebig's Letters on Chemistry, and Mr. J. Lloyd Bullock, one of Liebig's earlier pupils, and pointing out how very nearly a National Practical School of Chemistry became associated with the Royal Institution. After the failure of the negotiations with the Royal Institution, the agitation was continued, and ultimately, at a public meeting at the temporary offices of the College of Chemistry on July 29, 1845, a definite form was given to the proposed Institution, and a Council and Executive Officers were appointed, after which the first all-important subject to receive anxious consideration was the appointment of a Professor. The circumstances attending Hofmann's appointment were next referred to.

Temporary laboratories were fitted up in George Street. Twenty-six students entered in the first session, among whom were F. A. Abel, C. L. Bloxam, Warren De la Rue, R. Galloway, Henry How, E. C. Nicholson, and Thomas Rowney.

Hofmann's complete sway over his pupils, said Sir F. Abel, was at once secured by his indomitable perseverance and inexhaustible patience with the dullest, his earnestness of manner, his clearness of exposition, rendered additionally attractive by an inherent quaintness and a power of happily rendering German expressions into graphic English. Those first two sessions of the College, in the scantily equipped laboratories, with make-shift contrivances of the crudest character and an utter absence of any convenience for conducting investigations, must have been a sore trial of patience and powers of endurance to the impetuous young teacher, and to the enthusiastic worker, whose only recreation was the pursuit of original research. When to these circumstances is added the mental strain involved in the almost continuous pursuit of instruction and discussion in a foreign language, for at least eight hours daily, to say nothing of continued anxious consultations with the Council and officials of the College regarding ways and means; the heavy work connected with the erection and equipment of the permanent laboratories; the grappling with the problems of maintaining and fostering public interest in the Institution, and of keeping current expenses within very moderate bounds; it is self-evident that no small moral courage and powers of endurance were needed for the successful accomplishment of these duties; for the maintenance of the confident and apparently light-hearted demeanour, and of the power of instilling into others confidence of future success, which were peculiarly characteristic of Hofmann in those days of supreme difficulty. But these very characteristics, added to his genial and charming manner, high flow of spirits and originality in conversation and correspondence, secured to him devoted friends, not merely among colleagues snd pupils, but in whichever direction social intercourse was opened up to him. Just as his earnestness of purpose and enthusiasm kindled corresponding qualities in a large proportion of his pupils, so also his sanguine temperament and airy treatment of difficulties maintained, among many of the early friends and important patrons of the struggling Institution, a steadfastness of purpose which otherwise would doubtless have speedily waned.

Hofmann's method of teaching and his powers as a lecturer were next alluded to.

Thirty-seven students entered in the second session, making sixty-three in all, and the laboratories became inconveniently crowded. The third session was commenced in the new laboratories in Oxford Street in October, 1846. These included a small private laboratory for the Professor, and here Hofmann at once resumed research work, Nicholson acting as his assistant.

There is but one opinion among those who can appreciate the stupendous difficulty of the task so brilliantly accomplished by Hofmann, in placing the College of Chemistry upon a sure foundation, and in securing to it, within a very few years, a high position among the chemical schools of Europe—that his success was ascribable to the possession of a happy and rare combination of the highest talents as a teacher with exceptional powers as an investigator, inexhaustible industry and energy, and an enthusiasm not to be subdued by any obstacles—a characteristic quality possessed in the highest degree by his great master, Liebig.

The severity of work and many-sided training which those who assisted Hofmann in the early days of the College of Chemistry was illustrated by an account of Sir F. Abel's experience during five years as an assistant.

Sir F. Abel then referred to the more prominent pupils of Hofmann; to the character of the researches carried on in the College; to Hofmann's faculty of gauging the abilities and special qualifications of those who worked under him, and his power of directing and stimulating them; to his marvellous literary and linguistic skill; and to the ease with which he made friends. The pleasure with which he always referred to his career in London was illustrated by a letter addressed by Hofmann to the Prince of Wales, who, as President of the Society of Arts, wrote to him, in 1882, congratulating him on being the recipient of the Albert medal.

Dr. **Perkin** said that he was charged with the duty of giving an account of the rise and progress of the coal-tar colour industry, with which Hofmann's name was so inseparably connected, which he had been requested to make to a large extent autobiographical.

Aniline was Hofmann's first love, the subject of his first research, and he was the first to recognise the presence of benzene in coal-tar; in 1845, at his instigation, Charles Mansfield undertook the investigation of the coal-tar light oils, in the course of which he sacrificed his life, while obtaining results of the utmost value, both scientifically and technically. Dr. Perkin said that he entered as a student under Hofmann when in his 15th year, at the time when the Royal College of Chemistry became a part of the School of Mines: he soon got through the ordinary analytical course, and began to work at research—the problem which he was set by Hofmann to solve being to prepare a base from the hydrocarbon anthracene. Although the desired base was not obtained, the compound now known as anthraquinone was prepared, and also chloro- and bromo-derivatives of anthracene, but the results of the analyses were unintelligible, and it never occurred to them to doubt the correctness of Dumas and Laurent's formula for anthracene, $C_{15}H_{12}$. The experience thus gained, however, proved of great value later on.

When in his 17th year, he was promoted to the position of an assistant in the Research Laboratory, and as he had necessarily little time for private work in the day time, a room at home was roughly fitted up where he was able to work in the evenings and during vacations. Here a research was carried on jointly with Mr. Church, also an assistant in the Research Laboratory at the College, on some colouring matters derived from dinitrobenzene and dinitronaphthalene, in the course of which amidoazonaphthalene was prepared, which appears to have been the first compound obtained of the diazo-class shown to possess dyeing powers.

At about this time the artificial formation of natural organic substances attracted much attention, and Hofmann specially referred to the importance of preparing quinine in his report of the Royal College of Chemistry, pointing out that, judging from its composition, it might be a derivative of naphthylamine. Dr. Perkin said that as a young chemist he was ambitious to work on the subject, and, probably fired by Hofmann's remarks, began to think how quinine might be formed: it occurred to him that it might be produced by oxidising allyltoluidine, and experiments in this direction were accordingly made—needless to say, to no purpose, but the results led him to experiment on the oxidation of salts of aniline, and on using potassium bichromate a product was obtained containing among other substances the colouring matter afterwards known as aniline purple, Tyrian purple, or mauve. These experiments were made at home in the Easter vacation of 1856. In the summer vacation the preparation of the colouring matter was undertaken on a small technical scale in the back garden at home, and ultimately the process was patented on August 26, 1856. Not long afterwards, in conjunction with his father and brother, he commenced the manufacture of the dye. The extraordinary difficulties to be overcome were then referred to; not only had all the mechanical appliances to be devised, but at this time benzene was made in but small quantities and nitric acid of sufficient strength could not be procured commercially; moreover, methods of dyeing with the new colour had to be worked out.

Dr. Perkin then referred to the discovery of fuchsine (rosaniline) in France, and explained how Messrs. Simpson, Maule, and Nicholson, original manufacturers of fine chemicals, began its manufacture. Through Nicholson, Hofmann at this time exercised an all-important influence on the industry. Hofmann had always insisted on the absolute necessity of obtaining products in as nearly pure a condition as possible, and had thoroughly imbued Nicholson, who had carried out several investigations under him, with this idea; owing to Nicholson's skill, his firm soon succeeded in supplying fuchsine in a crystallised condition, and the example thus set has been of the greatest value.

Hofmann's own early investigations of rosaniline and its various derivatives were then referred to, and, after sketching the further developments of the industry, Dr. Perkin drew attention to Hofmann's various researches bearing on derivatives of coal-tar products.

In the latter part of his address he more briefly referred to the rise of the alizarin industry, pointing out that, although Hofmann had taken no part in this, it was undoubtedly the fact that his early introduction to anthracene, which he owed to Hofmann, was the cause of his becoming interested in the subject immediately Graebe and Liebermann's great discovery was announced. As in the case of the aniline colour industry, so in that of the alizarin industry, all the necessary machinery had to be devised, and many of the materials required had to be specially prepared for the purpose.

Hofmann's researches in connection with coal-tar colouring matters extended over a period of 25 years, from 1862 to 1887, and through these and the training which he imparted to those of his students who took part in the industry he exercised an influence unique in the history of modern industrial enterprise.

## PHYSICAL SOCIETY.

*Ordinary Meeting, May 20th, 1893.*

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Mr. C. J. Woodward showed some "*Experiments with a Vibrating Bar.*"

On suspending the bar by two loops of cord, and placing it over a resonance box, the sound was greatly intensified. When placed crosswise, and partly over the box, a position could be found where no increase of sound resulted, whilst a little movement in either direction from this position caused a considerable increase.

The discussion on Dr. Lodge's paper, "*The Foundation of Dynamics,*" was then resumed.

Communications on the subject from Mr. S. H. Burbury, Dr. J. Johnstone Stoney, and Prof. E. F. Herroun were read.

Mr. Burbury, referring to Dr. Lodge's deduction of conservation of energy on slip 6 of the paper, pointed out that two bodies may act on one another with equal and opposite forces and yet be moving with unequal velocities, and that the kinetic energy of such a system is not conserved. He did not see that denial of action at a distance was necessary to the proof given by the author.

Dr. Stoney said that only provisional and temporary foundations of dynamics could be deduced in the way followed by Dr. Lodge. It was necessary to first ascertain how the study of Nature is related to Ontology, but this essential, the author passed over by discarding metaphysics. When pursued in relation to the scientific study of Nature, Ontology throws a flood of light on most of the points dealt with in the paper.

Prof. Herroun considered that universal contact action involves the conception of a homogeneous ether filling all space, and yet having ordinary matter dispersed through it; this he regarded as a metaphysical impossibility. If the medium be supposed molecular, then action at a distance was only postponed one step. He thought Mr. Heaviside was right in denying the objectivity of energy, for it had no more claim to be regarded as an entity than "life" or "death," "hardness" or "colour," or any other generalised abstraction.

Prof. Minchin said the first fundamental axiom of dynamics postulates the existence of *force* as an entity distinct from *matter*, *space*, and *time*, and this was the object of Newton's First Law. It also gave the criterion of the presence of force. To merely retain the law as defining *equal times* was to degrade it. As regards the supposed impossibility of defining uniform motion, he said, similar difficulties occur in all sciences, even in geometry. Nevertheless, a rational science of geometry existed. In dynamics we had notions of a right line and of uniform motion in it, although no criterion of either may exist. The fact that the science harmonises with ordinary experience constitutes its validity. In his opinion the extraordinary devices which had been suggested for defining directions fixed in space were unnecessary, and merely served to cover the subject with ridicule.

He disagreed with Prof. Lodge in admitting the first law as a particular case of the second, for unless force was postulated (the function of the first law) the second became a mere definition, and not a law. Speaking of the third law, he said the author had made a serious error in stating that it could be deduced from the first, for the centre of mass of a system might be at rest without action and reaction necessarily being equal and opposite. The third law was not superfluous; neglecting it had led to great misconception and mystery about the principle of virtual work, and D'Alembert's principle, both of which are simple deductions from it.

In opposition to Dr. Lodge, he defended the ordinary definition of energy, and asserted that without the notion of *force* and *work*, the term *energy* loses all meaning.

Speaking of transference and transformation of energy, he inquired if the proof given could be applied to the case of a body sliding down a rough, rigid, inclined plane, for here the stress (friction) does work on the body but not on the plane, and there was no transference. He regretted that the expression "potential energy" was used in different senses in the paper, sometimes meaning "static energy," and at others "the available portion of the kinetic energy of a body."

Referring to the idea of all energy being ultimately kinetic, he asked if, by accepting this, the author meant to surrender the independent existence of force. If so, difficulties would arise; for example, in the kinetic theory of gases the expression for the pressure, $p = \frac{1}{3}\rho v^2$, was only arrived at by assuming the existence of force. The statement on the top of slip 9 about making a "moving body do work" was not necessarily true, as might be seen by considering the case of a sphere rolling down a rough inclined plane.

Prof. O. Henrici thought axioms should be treated as true logical definitions, as for example in geometry. "Two straight lines cannot enclose a space." Every new notion required its axiom. In passing from geometry to kinematics, the idea of time presented itself, and the appropriate axiom was contained in Newton's first law. On approaching dynamics, force and mass were met with. He disagreed with Prof. Minchin in regarding force as most fundamental. Mass was more essential, for force might be abolished. On the other hand, he concurred with Prof. Minchin in thinking that the idea of a centre of mass was not axiomatic. Referring to Dr. Lodge's summary (*Nature*, May 18, 1893), he agreed with axiom (*a*) fully, and with (*b*) partially. Axiom 3 required further development. The critical point, however, was axiom 4: "Stress cannot exist in or across empty space." This he regarded as very incomplete, and maintained that axioms defining the properties of the ether were necessary to further progress. If varieties of space be contemplated, each advance required fresh axioms.

Dr. C. V. Burton remarked that contact movement did not necessitate equal velocities; sliding motion was a case in point. Again, in deforming an incompressible fluid, although force and motion might exist, no work was done. Conservation could not be proved from denial of action at a distance. Speaking of the doctrine of transference and transformation of energy, he said it was a convenient working rule, but not true universally. Newton's laws were simple and consistent, but some doubt existed as to how much was definition and how much *law*, or fact.

Mr. Fournier d'Albe disagreed with Prof. Lodge in regarding the conception of uniform motion as a primary muscular sensation. It would be more correct to say that the conception was based on optical sensation, whilst the idea of force was derived from muscular sense. Newton's first law was not an axiom, for it could be proved experimentally. He thought Prof. Lodge's criterion of the identity of energy quite sufficient, if taken in conjunction with its conservation. The difference between the identity of energy and of matter lay in the number of attributes by which they could be identified, energy having only one, viz., quantity.

Prof. Ayrton said the best foundations of dynamics depended on what was most easy to grasp. On this point great difference of opinion existed; some persons thought the idea of *force* more simple than those of *mass* or *time*, whilst others had contrary impressions. He could not admit that the conservation of energy could be deduced from denial of action at a distance. Experiments were necessary. In addition to the case previously mentioned of a body sliding on a plane, he thought a hard magnet acted on by a coil approaching it and conveying a current, was one in which Prof. Lodge's law of transference and transformation did not hold.

Mr. Swinburne protested against difference between theory and a working hypothesis being overlooked. All conceptions were based on experience, and ideas of ether and atoms derived from "jelly" and "cricket balls." We ought also to remember what "explanation" means, viz., describing the unfamiliar in terms of the more familiar. It was customary to describe the phenomena of fluids by reference to solids, because we were more familiar with solids; an intellectual fish would probably do the reverse. The so-called "theory of magnetism" which breaks up a bar of iron into a number of small pieces, each possessing the properties of the original bar, he regarded as absurd. It was no "explanation" and not a "theory." Ether might be used as a working hypothesis, but must not be treated as an entity.

Mr. Blakesley questioned whether transference of energy was always accompanied by transformation, and he did not see why energy should be looked upon as—

$$(mv)\cdot\frac{v}{2},$$

in preference to any other subdivision of the factors. As regards effects being proportional to their causes, he pointed out that the heating of an electric circuit, and thermoelectric action, followed laws not linear.

Prof. S. P. Thompson, referring to the demonstration of the law of transference, &c., given on slip 8, said that attempts to translate it into Latin or Greek at once revealed the ambiguous character of the proof. Speaking of Ohm's law, he pointed out that R, a constant, was not an essential feature as Dr. Lodge supposed. Ohm never said R was constant.

In identifying energy, a difficulty presented itself, for one never came across it as a single thing, but as a product, and in being transformed the paths of the two factors might possibly be different.

Mr. Dickson said the whole of geometry and dynamics could be based on verbal definitions. The conservation of energy could be written as—

$$\text{Kinetic energy} + \text{potential energy} = \text{a constant},$$

but on substituting the expressions for kinetic and potential energies, an identity resulted; therefore the original statement was not a law. Both the kinetic and potential energies of a system were functions of its configuration. Potential energy could not belong to a particle but to a system.

The President doubted whether Dr. Lodge's scheme was more simple, natural, and logical than the ordinary one. The statement in *Nature* (May 18th) that "strains were proportional to stresses" was simple enough, but it was questionable if "frequency of vibration is independent of amplitude" could be considered so. The author appeared to ignore *mass* in comparison with *force*, whereas the idea of *mass* seemed the more simple one. Referring to the identity of energy, he said that however far we trace it, we cannot identify its parts in molecular structure. He objected to carrying too far the ideas derived from matter in mass, to particles, and pointed out that by so doing the difficulty was only pushed one step further and not cleared up.

Dr. Lodge, in reply to Mr. Burbury, said two bodies never do attract one another; the thing which acted on either was the medium immediately in contact with it. Mr. Herroun had used metaphysical arguments against ether, but he (Prof. Lodge) thought it was a good thing to investigate ether. He agreed with what Prof. Minchin said about force and the first law of motion. *Force* was the more fundament, but *mass* was best as a standard unit. As regards ether, he was prepared to say that it has no motion. It possessed electromagnetic kinetic energy, and probably all the stress energy that exists. Referring to the slipping body mentioned by Prof. Minchin and Dr. Burton, he said that in speaking of the velocities of acting and reacting bodies being equal, he always meant that their velocities along the line of action were equal. The action between the sliding body and plane was a "catch and let go" one, like a fiddle bow and string. On the second law of thermodynamics he hoped to say something in a subsequent paper. When he spoke of R being constant as the essence of Ohm's law, he meant constancy as regards terms which appear in the equation—

$$\frac{E}{C} = R.$$

## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, Monday, June 5, 1893.*

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—George Matthews Arnold, Charles Claude Carpenter, Frederick Henry Cheesewright, M.Inst.C.E., Ernest Prescot Hill, Henry Kemp, M.Inst.C.E., The Right Hon. Stuart Knill (Lord Mayor), Mrs. Lucas, Alexander Campbell Mackenzie, Mus. Doc., Carl Edward Melchers, Phineas Phillip, William Cuthbert Quilter, M.P., John Robbins, F.C.S., John Gorges Robinson, J.P., Thomas Thornton, and George White, B.A., LL.B.

The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—

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| Messrs. Crossley Bros. .. .. .. .. | £50 |
| James Mansergh .. .. .. .. .. .. | £21 |
| Sir Henry Doulton .. .. .. .. .. | £50 |
| Captain A. Noble.. .. .. .. .. .. | £50 |

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

**Microchemical Analysis of Rocks.**—Frey (*Pharm. Schweiz. Wochenschrift*) treats the minerals with hydrofluosilicic acid, and examines the silicofluorides produced. If, *e.g.*, a fragment of a sodiferous rock cemented with Canada balsam to a port-object is touched with a drop of pure hydrofluosilicic acid, there is formed sodium silicofluoride, which, on evaporation, leaves well-formed microscopic crystals of the hexagonal system, combinations of prisms, and pyramids. Potassiferous rocks yield small tesseral cubes, and calcium silicofluoride forms peculiar spindle-shaped tissues without plane boundary surfaces. In mixtures of silicates of these three elements there appear the different crystals in the exact proportion of the bases in the rock. Iron, manganese, and magnesium can be distinguished in a similar manner. These silicofluorides are certainly very similar, but if treated with chlorine the iron crystals turn yellow, those of manganese red, whilst those of magnesium remain colourless.

## NOTICES OF BOOKS.

*City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors.* April, 1893. Gresham College, Basinghall Street.

This report presents along with some very satisfactory features certain others which are less reassuring. On the one hand, it is pleasant to note that the number of day students has increased from 382 in the past Session to 412 in the current Session; that "the nature of the instruction both in the day and evening departments consists to a very large extent in practical work. Students spend the greater part of their time in the laboratories and workshops, and receive individual instruction and supervision."

It is satisfactory to find that some of the former students are now filling important positions in industrial establishments, and are capable of effecting real improvements. Even one such fact is a result of more importance than ten thousand successful examinations.

A less satisfactory feature is that the Corporation of London have withdrawn their financial support from the Institute. We are not disposed to believe that the Corporation has become indifferent to the importance of technical education, but the rumours of confiscation vented in different quarters have a necessarily restricting action upon munificence, whether private or corporate.

Another disappointing feature is the relatively small number of students who devote themselves to chemistry. At the Central Institution the numbers of students in chemistry for the Sessions 1890—91, 1891—92, and for the winter term of 1892, have been 12, 11, and 10; whilst the total of students in all four departments has been respectively 144, 160, and 172. Thus it will be at once seen that the number of chemistry students has declined not merely positively but relatively.

In the Finsbury Technical College the chemistry students have during the past three sessions increased from 37 to 41; small figures out of totals of 184, 198, and 213. An honour gained by this college is that Mr. H. D. Richmond, one of their former students, now Analyst to the Egyptian Government, is the discoverer of the new element masrium.

In the Evening Department chemistry comes out even worse. The number of students for the Session 1890—91 was 6 out of a total of 334, and that for 1891—92 7 out of 329! These figures are the more discouraging as the two Professors—H. E. Armstrong at the Central Institution, and R. Meldola at the Finsbury Technical College—are both decidedly "the right men in the right places."

Of course, it must be recognised that, as in all British educational institutions, examinations play far too prominent a part. The warnings of Mr. Auberon Herbert and his friends are as little noticed as those of Cassandra of old.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 20, May 15, 1893.

**Determination of Boron.**—Henri Moissan.—This paper will be inserted in full.

**The Cultivation of the Soil and Nitrification.**—P. P. Dehérain.—This paper also will be inserted at considerable length.

**A Study of the Cadmium and Sal-ammoniac Battery.**—A. Ditte.—Cadmium, in the cold, has no action on a solution of ammonium chloride, but its oxide may combine with this chloride, yielding transparent crystals decomposable by water and containing $2(NH_4Cl)CdO$. The electrolysis of a solution of sal-ammoniac under the electromotive action which ensues on the contact of a platinum-cadmium couple immersed in this liquid is still exothermic. In all the batteries examined the fundamental action is always an exothermic electrolysis of the saline solution yielding alkali and chlorine, which forms with the metal the corresponding chloride. The liquid is not homogeneous at all depths; it is more alkaline in its upper strata, and contains towards the bottom more cadmium (or zinc) chloride.

**Influence of the Temperature of Re-Heating upon the Mechanical Properties and the Structure of Brass.**—Georges Charpy.—The author proposes to study the modification of these properties as a function of the temperature of re-heating, and to examine if this phenomenon can be ascribed to an alteration of the structure of the alloy. His researches have hitherto been confined to a brass consisting of 67 parts of copper and 33 of zinc. It appears that in general brass is formed of two distinct alloys, the one crystalline and the other amorphous, playing the part of a cement. In the case of brass crystallisation improves the mechanical properties of the metal.

**On Substituted Malic Acids.**—Ph. A. Guye.—This paper may be regarded as an appendix to M. Colson's controversy with M. Friedel and M. Le Bel.

**Action of Zinc Chloride upon Chloro-Camphor. Relation between Camphor and Carvacrol.**—A. Etard. Carvol hydrochlorate behaves as a phenolic addition product, for it is split up by simple distillation (with or without zinc chloride) into carvacrol and HCl. Chloro-camphor behaves in the same manner as a carvacrol hydrochlorate. As a chemical function camphor may be regarded as a hydro-carvacrol.

**A Certain Number of Organo-Metallic Compounds belonging to the Aromatic Series.**—G. Perrier.—The compounds in question are aluminium chloride with ethers, with the acetone phenols, and with the phenols.

**Inulase and the Indirect Alcoholic Fermentation of Inuline.**—E. Bourquelot.—In many plants of the family of the Compositæ, especially in dahlias, the carbohydrate in reserve is not starch but inuline. Chemically these compounds differ by the circumstance that if treated by boiling dilute acids starch yields dextrose, whilst inuline produces levulose. From a physiological point of view they play the same part. It has long been known that the saccharification of starch is effected by a soluble ferment, diastase. It has been lately discovered by J. R. Green that the corresponding agent for inuline is inulase. Instead of using dilute sulphuric acid for converting inuline into a fermentible sugar the process may be effected by means of pure cultures of *Aspergillus niger*.

**Contribution to the Study of the Chemical Phenomena of the Assimilation of Carbonic Acid by Chlorophyllaceous Plants.**—A. Bach.—The author considers that the splitting up of hydrated carbonic acid, $CO_3H_2$, follows a course analogous to the splitting up of sulphurous acid on exposure to solar radiation.

## MEETINGS FOR THE WEEK.

Tuesday, 13th.—Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
Thursday, 15th.—Royal, 4.30.
—— Chemical, 8, "Contributions to our Knowledge of the Aconite Alkaloids" (VI. Conversion of Aconitine into Isaconitine, by Prof. Dunstan and Mr. F. H. Carr; VII. Modifications of Aconitine Aurochloride, by Prof. Dunstan and Mr. H. A. D. Jowett. "Properties of Strong Solutions," and "Note on the Stereoisomerism of Nitrogen Compounds," by S. U. Pickering, F.R.S. And other papers.
Friday, 16th.—Quekett Club, 8.

## TO CORRESPONDENTS.

*R. B.*—In most cases ammonium acetate will answer as well as sodium acetate. When, however, continuous boiling is required, the sodium salt is preferred, as it does not decompose and lose acid so readily as the ammonium salt. We know no better book on the subject of Bread and Flour than the one by Jago.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1751.

## FLAME SPECTRA AT HIGH TEMPERATURES.*

### Part I. Oxyhydrogen Blowpipe Spectra.

By W. N. HARTLEY, F.R.S.

Brewster, in 1842, first examined the spectra of salts with a flame of oxygen and coal-gas (*Proc. Roy. Soc. Edin.*, vi., p. 145).

Professor Norman Lockyer has given us maps of twenty-two metallic spectra at the temperature of the oxygen and coal-gas flame. The region observed lies between λ 7000 and 4000.

Preparatory to undertaking the study of spectroscopic phenomena connected with the Bessemer "blow" and the manufacture of steel generally, I have carefully observed the spectra of metals and metallic oxides obtained by submitting the substances to the oxyhydrogen flame.

*Method of Investigation.*—The method of obtaining spectra with flames at high temperatures is the following. Hydrogen proceeding from a large lead generator is burnt in a blowpipe with compressed oxygen. The blowpipe measures 3 in. in length by $\frac{3}{8}$ in. external diameter. The substances examined are supported in the flame on small plates of kyanite about 2 in. in length, $\frac{1}{20}$ in. in thickness, and $\frac{1}{4}$ in. in width. This mineral, which is found in masses in co. Donegal, contains 96 per cent of aluminium silicate, and is practically infusible. The spectra were all photographed with the instrument employed by me on former occasions for photographing ultra-violet spectra, illustrations of which were published in the *Chem. Soc. Journ.*, xli., p. 91, 1882. The dispersion of the instrument was that of one quartz prism of 60°.

Isochromatic plates developed with hydroquinone were largely used. Various dyes for sensitising and all kinds of developing substances were tried. The spectra were measured with an ivory scale divided into hundredths of an inch, and directly applied to the photographs, the division 20 on the scale being made to coincide with the yellow sodium line which appears in every photograph. It was found convenient to record the measurements on a gelatino-bromide paper print taken from an enlarged negative. Sometimes, for more careful and minute reference, it was found convenient to make an enlargement of the spectrum with the scale in position, but accurate measurements cannot be made in this way. It is necessary to use a low magnifying power and cross wires in the eye-piece.

For the identification of lines already known nothing more complicated is required, but to measure new lines and bands it was considered desirable to make use of a micrometer and microscope; the screw of the micrometer was cut with 100 threads to the inch, and the magnifying power generally used was 10 diameters.

*Characters and Extent of the Spectra Observed.*—Just as in the ordinary use of the spectroscope we must be prepared to see the lines of sodium, and in hydrocarbon flames the bands of carbon, so in these spectra the sodium lines and the strongest lines belonging to the emission spectrum of water vapour are also always present.

In addition, tha kyanite yields the red line of lithium, which is no inconvenience, but a positive advantage, serving, as it does, to indicate where the spectra commence.

A large majority of the metals and their compounds all terminate somewhere about the strongest series of water vapour lines. Typical non-metallic spectra are sulphur, selenium, and tellurium; the first yields a continuous spectrum with a series of beautiful fluted bands, the second a series of fine bands occurring at closer intervals, and the third is characterised by bands still closer together, and near the more refrangible termination of which four lines occurring in Hartley and Adeney's spark spectrum of tellurium are visible. Increase in atomic mass causes shorter periods of recurrence of bands. In line spectra it is the reverse; increase in atomic mass causes greater periods in the recurrence of lines. Charcoal and carbon monoxide yield chiefly continuous spectra; the latter, however, exhibits some carbon lines. The hydrocarbons yield the well-known spectrum of carbon bands with also those attributed to cyanogen. Of metallic elements, nickel, chromium, and cobalt yield purely line spectra; antimony, bismuth, silver, tin, lead, and gold beautiful banded spectra (spectra of the first order) accompanied by some few lines. These spectra are finer than those of selenium and tellurium.

Iron and copper exhibit lines and, less prominently, bands. Manganese has a beautiful series of bands and a group of three very closely adjacent lines. Aluminium gives a fine continuous spectrum with three lines, origin uncertain, zinc a continuous spectrum without lines, and cadmium a spectrum consisting of one single line only, λ 3260·2.

Of compounds, chromic trioxide yields a continuous spectrum with six lines belonging to the metal, copper oxide a fine band spectrum with two lines of the metal, magnesium sulphate gives a spectrum of magnesium oxide consisting of broad degraded bands composed of closely adjacent fine lines and one line belonging to the metal, λ 2852.

The sulphates of calcium, strontium, and barium give both bands of the oxides and lines of the elements. Phosphorus pentoxide yields a continuous spectrum with one peculiar line, seen also in the spectrum of arsenic.

The chlorides of the alkalis give also lines of the elements with a more or less continuous spectrum, which, it is believed, is due to the metal in each case. Lithium chloride gives no continuous spectrum.

*The Volatility of Metals.*—One of the most interesting facts ascertained by this investigation is the volatility of all the metals examined, except platinum, and particularly the extraordinary volatility of manganese, and, to some extent, of the infusible metal iridium. Metal believed to be pure iridium is seen to have diminished after the flame has played upon it for about two hours.

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## ATTEMPT AT A GENERAL METHOD OF CHEMICAL SYNTHESIS.

By RAOUL PICTET.

In order to develope from the totality of facts explained in my former papers a practical method of utilising low temperatures in chemical syntheses, it will be useful to recal the partial laws which we have already seen.

The fundamental hypothesis which has guided us and the experimental verifications have enabled us to establish eight laws:—

1. At very low temperatures, below −130°, no chemical reaction takes place, whatever substances are present.

2. All chemical reactions are manifested spontaneously at a certain temperature and under a certain pressure exerted upon the constituents; this is the temperature limit.

3. The same reactions may be obtained below the temperature limit if we apply auxiliary energy by the use of electric currents or discharges.

4. Exothermic reactions always present two phases: in the former we retain a control of the temperatures if we can remove from the combining bodies, by radiation, as

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* Abstract of a Paper read before the Royal Society, June 1, 1893.

much heat as is produced at the same moment by the simultaneous effect of the affinities of the extraneous energies introduced into the substances. In the second phase, the temperature rises suddenly until the reaction takes place above the temperature limit.

The first phase is the reaction limit. The second phase is the reaction in mass.

5. Endothermic reactions are always limit reactions.

6. The dissociation of the products obtained by exothermic reactions corresponds to the laws of endothermic combinations and reciprocally.

7. The temperature limit of chemical reactions is not in a known simple relation with the apparent energy of the phenomenon. On the contrary, the quantities of heat liberated seem to class the ascending order of the temperature limit, especially in one and the same family of substances.

8. The electric spark and current seem to be the best media for supplying extraneous energy to limited chemical reactions.

With these eight partial laws we may establish a complete scientific programme for the discovery of a general method of chemical synthesis.

We begin by bringing in contact the simple bodies, and defining experimentally the laws which govern their combinations, the relations between their temperatures, the pressures, and the quantities of heat to be supplied in limited reactions.

As this first series of observations, must, on principle, give precise numerical values, we must never allow reactions in mass to interfere, as they disturb and modify the thermic conditions of the phenomenon. This condition, *sine qua non*, indicates at once the plan of operations to be followed. The chemist must have at command a powerful refrigeratory apparatus, by which he can at least reach temperatures of −130° to −150°, so as to paralyse all chemical reaction. Substances thus cooled are certainly below all the temperature limits.

The refrigerating tank must have a temperature which can be regulated at will from −130° to the ordinary temperature.

A powerful induction coil yields sparks which must be made to strike, by means of insulated conductors through the substances to be combined, in the refrigerated enclosure.

When the reaction commences, the heat produced each moment by the weight of the compounds obtained must be withdrawn by radiation, so that the temperature at which the reaction is produced may be kept constant.

The quantities of energy represented by the electric current in ampères and volts are equivalent to the endothermic phase of the reaction. The quantities of heat lost by radiation measure the exothermic phase.

The calorimetric measure effected in the refrigeratory enables us to know directly the effect of radiation for all the differences of temperature.

We shall on this principle constitute the first rational dynamic table in chemistry, by studying all the simple bodies, two by two, three by three, &c. By combining by the same methods, and with the same appliances, the binary bodies with the simple bodies, we obtain the second dynamic table. Next we pass to the ternary substances, &c.

The successive experiments will discover the laws which govern the phenomena, and will in so far facilitate the knowledge of the utilisation of the dynamic tables.

The line of the greatest chemical declination of all bodies will thus be determined experimentally.

Chemical reactions will be defined in a manner as precise and certain as the fall of a body on an inclined plane by a single track without ambiguity. We shall know beforehand, for any reaction which we may wish to produce, all the conditions to be fulfilled so as to obtain only a single effect, *e.g.*, the fixation of a new element upon a given primitive nucleus.

The track will be known and the result certain. Under this form we see the possibility of forming rationally by direct synthesis all the substances in nature.

It is probable that along with the electric spark we may utilise other sources of auxiliary energy, *e.g.*, the collateral chemical reactions produced in the series of substances studied, and which will yield a known number of calories. The subject of this immense research is scarcely touched upon; we have confined ourselves to lay down its principal lines.

The present experimental results give a preliminary sanction to this programme.

In concluding the exposition of these general views on the phenomena of ponderable matter, we see that the same equations of motion may represent as a simple function of distances:—

1. All astronomy and the phenomena of gravitation, the distance of bodies which attract each other, passing from infinity to distances where the action of the ether manifests itself to modify the law of Newton.

2. All cohesion where the totality of the physical phenomena of changes of state linked to calorific phenomena where the distances of the attracting bodies pass from the limits of gravitation to the distance of bodies refrigerated to the absolute zero.

3. All chemistry, phenomena of motion, when the distance of the attracting bodies is smaller than that observed at the absolute zero.

The equations of the movement of matter permit us thus to reduce these three sciences to a single formula, the numerical terms of which are not yet known, but from which we may logically deduce every observable phenomenon.—*Comptes Rendus*, cxvi., p. 1057.

## A NEW METHOD FOR DETERMINING THE FATTY MATTER OF MILK.

By LEO. LIEBERMANN and S. SZÉKELY.

Most of the better-known methods of determining the fat of milk, if they do not depend on purely physical principles, use ether as a solvent. None of these methods can be perfectly accurate, since ether, in addition to milk-fat, takes up other substances. This observation is not quite new; it was pointed out some time ago by one of the present writers (*Pharm. Centralhalle*, 1885), and has been noticed elsewhere, but it has not been utilised for an exact determination of the fat of milk.

It appears from the following experiments that the errors thus occasioned are not quite insignificant:—

The fat of a milk was determined according to the well-known method of Adams. We took the precaution of previously saturating the specially prepared commercial slips of paper with acid sodium phosphate (for the more ready elimination of any resinous acids present), and extracting them with ether. The fat obtained from the milk was dried and again dissolved in ether, when it was found that on this second solution a certain portion was not taken up by the ether. We filtered the ethereal solution, carefully washed the filter with ether, and after the expulsion of the ether we weighed the residue again.

In the first weighing we obtained 3·60 per cent; in the second, though all loss was carefully avoided, only 3·35 per cent. The difference was therefore 0·25 per cent, which did not consist of fat.

In a second portion of the same milk we again determined the fat by the Adams' method, extracting, however, with petroleum ether instead of with ether. We obtained 3·40 per cent fat. We have thus a proof that the first extraction with ether did not give an accurate result. The second result, obtained by re-dissolving the dried milk-fat, was correct, since the difference was only 0·05 per cent.

The fat was also determined in the same milk by Soxhlet's aræometric process and by Hoppe Seyler's method; the former process gave 3·69 per cent and the latter 3·85 per cent.

In a second experiment we obtained, on extraction with ether (Adams), 3·96 per cent, and on extracting the milk previously desiccated with sand 4·07 per cent. In both cases, on again dissolving, we found a residue insoluble in ether, after the removal of which the quantity of fat obtained according to Adams was reduced from 3·96 to 3·86 per cent; whilst the portion treated by the other process fell from 4·07 to 3·95 per cent. The same milk on extraction with petroleum ether gave 3·78 per cent of fat.

It is remarkable that the fats extracted respectively with ether or petroleum ether often differ in their outward appearance. The residue from ether is, as a rule, yellowish; that from petroleum ether pure white and perfectly soluble in the solvents of the fatty matters.

We instituted an entire series of comparative experiments, from which it appears, without exception, that higher percentages are always obtained with ether than with petroleum ether. These differences are so considerable that they cannot be explained by an excess of matter extracted by the ether from the prepared paper or from the impurities of the gypsum or the sand. It is certainly for the greatest part derived from the milk itself. We have found that the paper prepared for the Adams method yielded to ether only 0·002 grm., whilst sand and gypsum gave off only 0·011 grm.

We have further made comparative experiments with the method proposed some time ago by one of us (Liebermann), and with the method as modified by Wolff.

We found in a milk:—

| | |
|---|---|
| According to Adams, with ether .. .. | =3·91 p. c. |
| ,, Liebermann .. .. .. | =4·12 ,, |
| With Wolff's modification .. .. .. | =3·97 ,, |
| Extraction with petroleum ether (Adams) | =3·77 ,, |

In another milk:—

| | |
|---|---|
| According to Adams, with ether .. .. | =5·55 p. c. |
| ,, Liebermann .. .. .. | =5·32 ,, |
| Wolff's modification .. .. .. .. | =5·17 ,, |
| Adams, with petroleum ether .. .. | =5·07 ,, |

Considering that the differences on using petroleum ether are not unimportant, amounting on the average to 0·17 per cent, but in some cases exceeding 0·4 per cent, we consider ether unfit for the accurate determination of milk-fat, and recommend in its place light petroleum ether.

At the same time we propose a new, convenient, and accurate method, a further development of that which one of us (Liebermann) published some time ago (*Zeit. Anal. Chemie*, xxii., 383, and xxiii., 476).

### *The New Method.*

Fifty c.c. milk at the temperature of the room are put in a glass cylinder about 25 c.m. in height and about 4½ c.m. internal diameter; there are added 5 c.c. of potassa-lye at 1·27 specific gravity, closed with a well-fitting cork, and well shaken.

To this mixture are added 50 c.c. of a light petroleum ether, the specific gravity of which is about 0·663, the boiling-point 60°, and which evaporates on the water-bath without residue. The glass is stoppered, and again vigorously shaken so as to form an emulsion. To this emulsion are added 50 c.c. alcohol of about 95·8 to 96 per cent, and the liquid is again well shaken. After at most four or five minutes the petroleum ether separates at the top, and the separation may be regarded as complete. We shake again three or four times, each time for a quarter of a minute, allowing each time the ether to separate out.

The petroleum ether will now have taken up all the fat. We ascertained this point by shaking up eleven specimens a different number of times, the first once and the eleventh eleven times. Already after the third and fourth shaking we have found quantities of fat which differ from each other only to an unimportant degree. After once shaking 3·535 per cent, after twice shaking 3·54 per cent, and the results which we obtained between the third and the eleventh shaking fluctuated only between 3·55 and 3·56 per cent.

Of the stratum of petroleum ether, 20 c.c. are drawn off with a pipette and introduced into a small tared capsule, the capacity of which is about 40 to 50 c.c., and the neck of which is higher than 1 c m., with a diameter of 1½ to 2 c.m. These small flasks are convenient, because the liquid does not readily rise out of them, and yet the evaporation goes on with sufficient rapidity. But of course small tared beakers or ordinary flasks may be used.

The flask is set upon a water-bath at a moderate heat, the petroleum ether is evaporated entirely away, and the residue is dried at from 110° to 120°, for which an hour is generally sufficient; the weight found, if multiplied by 5, gives the quantity of fat in 100 c.c.

The quantities of fat obtained by the new method may be easily re-calculated by the aid of the specific gravity into percentages by weight, so as to admit of a comparison with the Adams method, in which the milk is weighed. We remark that on the Adams method the extraction with petroleum ether must last for at least 3 hours.

The results of the new method vary from those of the gravimetric method by 0·066 in a positive direction, and by 0·037 per cent in a negative direction. But these deviations, in our opinion, are not necessarily founded on sources of error in the method, but are chiefly due to the circumstance that in the gravimetric method the milk is weighed, whilst in the new method it is measured, and that the re-calculation may occasion errors.—*Zeitschrift f. Anal. Chemie*, xxxv., p. 168.

## PROGRESS OF CHEMISTRY AS DEPICTED IN APPARATUS AND LABORATORIES.*

By H. CARRINGTON BOLTON.

(Concluded from p. 272).

A special form of furnace much extolled for alchemical operations was an "athanor," deathless, because the fire could be maintained indefinitely. The residuum of any distillation was a "caput mortuum," death's head. A cone-shaped bag for filtering was early known as "Hippocrates' sleeve"; the operating of closing a flask by fusing the neck was applying the "seal of Hermes"; fusing of two metals was their "marriage." A still more extravagant nomenclature was applied to chemical substances themselves, but of these and of the characters employed to designate them I have already addressed the Academy (December 11, 1882, and March 12, 1883). A single example will suffice. Basil Valentine wrote: "The greater the quantity of the eagle opposed to the lion the shorter the combat; torment the lion until he is weary and desires death. Make as much of eagle until it weeps, collect the tears and the blood of the lion and mix them in the philosophical vase." That is to say: "Dissolve the substance and volatilize it."

In Iheronimus Brunschwick's *Liber de arte distillandi compositis* (1500) are many coarse woodcuts representing distillations conducted under different planetary aspects; also a noteworthy interior of a pharmacy of the fifteenth century, the apothecary's assistant busy with a pestle, gallipots on shelves, scales on a hook, and the licence and certificates of the master conspicuously displayed.

The remarkable and abundant illustrations of the

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* (Abstract). From the *Transactions of the New York Academy of Sciences*, Vol. XII.

operations of mining, treatment of ores by washing and smelting, in George Agricola's *De re metallica* (1556), are too well known to need mention.

The *Alchymia* of Andreas Libau (or Libavius), published at Frankfort in 1595, is conspicuous for accuracy of description and systematic arrangement of topics. He treats in this work of the *Encheria*, or manual operations, and of the *Chymia*, or substances, in separate books. The former he divides into two sections, one dealing with laboratory apparatus, and one with the construction and management of furnaces. He describes and figures an ideal laboratory provided not only with every requisite for chemical experimentation, but also the means of entertaining visitors, including such luxuries as baths, enclosed corridors for exercise in inclement weather, and a well stocked wine-cellar. This work, sometimes called the "First Text-book of Chemistry," contains woodcuts of a great variety of alembics having peculiar forms for special uses; also a distilling apparatus fitted with an ingenious system of condensers for very volatile liquids. Besides the usual funnels for filtering Libavius describes the now neglected method of filtering by capillary fibres of wool or asbestus; a process which, however, was known as early as 400 B.C., as I have shown in a paper read to the Academy Oct. 13, 1879. Filtration was often styled "destillatio per filtrum," and the method just named was known as "destillatio per lacinias;" it is practically capillary syphoning.

Libavius' sumptuous plans were never realised, but towards the close of the seventeenth century the first public laboratory was opened at Altdorf (near Nuremberg) under Prof. John Moritz Hoffman. In the same year (1683), the first government laboratory was established by Karl XI. at Stockholm; of this the first director was Urban Hjärne.

A woodcut in a work published in 1570 depicts in a very interesting way all the steps in the manufacture of sugar, men chopping the cane, others grinding and pressing it, large cauldrons for boiling the juice, conical moulds in a frame, and the completed sugar-loafs.

Distilling apparatus in great variety is figured in the *Elixir vitæ* of the Italian author Donato d'Eremita, published in 1624. This pharmaceutical work contains nineteen full-page plates engraved with delicate skill.

In Kircher's *Mundus Subterraneus* (1665) are engraved numerous forms of furnaces and stillatories, largely copied from Donato d'Eremita's work.

J. J. Becher, in his account of a "Portable laboratory" (1719), exhibits on a single plate sixty-four different articles, including the following: Crucibles, muffles, cupels or tests, moulds for making cupels and for casting metals, mortars, mills for grinding, bellows, tongs, forceps, a tripod for supporting dishes, a rabbits-foot for brushing powders, a hand screen to protect the face from heat, various vessels of wood, copper, and iron, scales for weighing (three styles), retorts, phials, funnels, bladders, besides an apron, a towel, a linen jacket, an hour-glass, candles, and tobacco-pipes!

Straw-rings for supporting round-bottomed vessels are pictured in Lefevre's *Traité* (1669).

The interior of the University laboratory at Utrecht, under the direction of Johann Conrad Barchusen, Professor of Medicine and Chemistry, is neatly figured in his *Pyrosophia*, published 1698. In this, as in others of the period, the prominence given to furnaces reflects the importance attributed to operations by fire.

Physical instruments of chemical application were slower in developing; thermoscopes appeared early in the seventeenth century, and thermometers somewhat later.* Torricelli discovered the barometer in 1643, and Pascal tested its utility on the Puy-de-Dôme five years later.

Otto de Guericke's air-pump and frictional electric machine, together with the interesting experiments conducted with the Magdeburg hemispheres, are handsomely depicted in his celebrated treatise *De vacuo spatio*, published in 1672. This air pump and the hemispheres are preserved in the Royal Library, Berlin. The Hon. Robert Boyle improved Guericke's air pump in 1659, and used it in laying the foundations of pneumatic chemistry, a field that from this time occupies our attention almost exclusively. Boyle's air pump and accessory apparatus are figured in plates accompanying the several editions of his works.

As is well known, the earlier chemists paid little or no attention to gases, though they were familiar with processes which generated them; perhaps the study of gases was retarded by lack of inventive skill in handling them. Dr. Beddoes, writing of Mayow, and reflecting on this point, uses the following language: "To be sensible of the merit of these contrivances of Mayow, we have only to recollect how difficult it must have appeared to confine, divide, remove from vessel to vessel, examine, and manage at pleasure fugitive, incoercible, and impalpable fluids like that which we breathe."

In 1672 Boyle obtained hydrogen gas by the action of acids on iron filings, and showed its combustibility, but seems to have made no attempt to collect and examine the gas.

The first scientific experiments in pneumatic chemistry were made by John Mayow, an Oxford physician, born in 1645 and died at the age of 34 years. In 1669 he published a work entitled *De sal-nitro et spiritu nitro-aëreo*, in which he figures his apparatus and describes his methods. To confine and study any gas, the air, for example, he inverted a cucurbit in a pan of water, used a syphon to establish the level of the water within and without, and introduced a shelf into the wider part of the cucurbit, from which he hung substances whose action he examined. He used a burning glass to ignite substances, camphor for example, placed in the cucurbit; he also introduced a mouse in a cage supported on a tripod under the cucurbit. He adopted an ingenious plan for transfering gases from one vessel to another, shown in the engraving that accompanies his rare treatises. Mayow failed to distinguish different gases, but was the pioneer in the method of manipulating them. Of his anticipating later theories of combustion we make mere mention, as our theme excludes theory.

Mayow's contrivances were somewhat improved by the eminent English botanist, Rev. Dr. Stephen Hales. In his "Vegetable Statics" (1727) he describes an attempt to analyse the air with many ingenious devices. Hales heated substances in a retort communicating by means of a syphon with a receiver consisting of a flask inverted in a vessel of water, the flask being supported by a cord from above. He heated nitre in this way, and especially noted the permanency of the air obtained, but failed to examine the properties of the air; and he failed to differentiate the several gases obtained by his methods.

Even before Hales, however, an obscure physician in France, Moitrel d'Elément, had invented improved methods of handling gases. In 1719 he published a little pamphlet containing lucid instructions for measuring and collecting gases; especially noteworthy is the separation of generator and receiver first suggested by him. The poor physician's skill was unnoticed by his contemporaries. In his old age a benevolent person took him to America, where he died unhonoured and unsung.

In 1757 Professor Joseph Black, of Scotland, determined the true characteristics of "fixed air," but seems to have made no important addition to the apparatus for studying gases.

In 1767 Mr. Peter Woulfe published a paper in the *Phil. Trans.* describing an improved apparatus for condensing vapours without loss, and applied it to hydrochloric acid, ammonia, nitric acid, and other

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* Geber remarks that "Fire is not a thing which can be measured, therefore it happens that error is often committed in it." He evidently felt the need of thermometers.

substances obtained by distillation. The apparatus still bears his name.

The prodigious advance made by Dr. Joseph Priestley in the manipulation of gases won for him the appellation "Father of Pneumatic Chemistry." His prime invention was the insertion of a shelf into the vessel containing water, and the perforation of this shelf so as to admit of the gases ascending into receivers standing thereupon. This pnuematic trough is not mentioned by Priestley in his first chemical paper, published in 1772, entitled "Directions for Impregnating Water with Fixed Air." In this tract the accompanying figures illustrate his method of collecting the gases. A bottle for generating the carbonic acid, to the mouth of which is attached a bladder, and this in turn communicates with an inverted jar by a flexible "leather pipe sewn with waxed thread" and having quills thrust in both ends to keep them open. This simple apparatus was the forerunner of the modern soda-water machines.

In the first edition of Vol. I. of Priestley's "Experiments and Observations on Different Kind of Air," published two years later than the little treatise above noticed, the author modestly says "my apparatus for experiments on air is in fact nothing more than the apparatus of Dr. Hales, Dr. Brownrigg, and Mr. Cavendish, diversified and made a little more simple." He then describes the pnuematic trough, both for water and for quicksilver, the method of pouring air upward under water, the process of generating gases by heating substances in a gunbarrel, by aid of a burning glass in thin phials filled with quicksilver, and the way to pass an electric spark through gases in a jar over water or over quicksilver. This introductory chapter clearly shows the greatest progress in the manipulation of gases, and the way in which Priestley energetically applied his skill by the discovery of nine gases is well known to every student.

After the disastrous riots in Birmingham, July, 1791, in which Priestley's house and laboratory were wholly destroyed by an angry mob, an inventory was taken of Priestley's laboratory as a basis for damages. This inventory has been preserved, and affords detailed knowledge of the material resources of the chemists of the period. It is divided into groups, philosophical instruments, electrical, optical, mathematical, and chemical apparatus, with a small stock of substances, the whole footing up to the value of £605. The imperfections of some of the apparatus used by Priestley are shown by the fact that he experimented from December, 1782, to May, 1713, on the direct conversion of water into air by distillation only without the intervention of any other substance, to discover after all that this astonishing result was due solely to leaks in the porous earthen retorts employed in the process. The retorts, as well as other articles, had been supplied gratis by Joseph Wedgwood; and Priestley, writing for more, desired to have them glazed within and without. (Scientific Correspondence of Priestley. New York, 1892.)

Scheele, the poor apothecary in a little village of remote Sweden, had to contend with obstacles sufficient to crush any but the bravest heart. With a few bottles, bladders, common dishes, and the simple appliances of a primitive pharmacy, this man of expedients accomplished wonders. Scheele's apparatus for generating oxygen was a simple retort, to the neck of which he tied a bladder. He was not acquainted with the pneumatic trough at the time of his chief discoveries. (Scheele's "Air and Fire." London, 1780.)

In 1796 James Watt, the English engineer, published an account of a simplified "Pneumatic Apparatus for Preparing Factitious Airs." In this is figured an "air-holder" made of tin-plate japanned inside and out, into which gas is conducted from the generating retort in a furnace, by means of a metallic tube bent at an angle of 45°, and terminating in the air-holder. Watt lays great stress on the advantages of inclining the "lower pipe," as stated, though Hales certainly anticipated him in this point. This pneumatic apparatus was manufactured by Boulton and Watt, at Soho, in two forms; a large size sold for £10 2s. 6d., including auxiliary articles, and a portable apparatus for £3 15s. The pamphlet states that this apparatus are especially adapted for procuring "hydrocarbonate and oxygen air."

Meanwhile, across the Channel, in Paris, the opulent physicist and chemist, the unfortunate Lavoisier, enjoyed the advantages of highly specialised and admirably constructed apparatus of every description. An inspection of the plates in the *Traite élémentaire de chimie* (1798) shows what a wealth or excellent utensils he had at his command. Two sketches by the pencil of Mme. Lavoisier introduce us into his laboratory while he is conducting experiments in the respiration of a man at work and of a man in repose. After Lavoisier's legalised murder, an inventory of his laboratory was made by a government commission, among whom was the distinguished Nicholas Leblanc.

Accurate balances now became most important adjuncts to chemical laboratories.

Towards the close of the last century Italy contributed chemical research to two inventions of marvellous power—the Galvanic trough and the Voltaic pile, destined to electrify material human progress.

To sketch the development of chemical apparatus in this century would prolong this superficial review unnecessarily; modern appliances are distinguished by careful adaptation of the means to the end, and are improved by the introduction of coal-gas for heating purposes, by the use of india-rubber tubing and platinum vessels, and by the delicate products of the glass blowers' skill. To these features may be added novel contrivances for analytical chemistry, a field too recent to require elucidation.

(The paper was illustrated with 80 lantern views of the apparatus and laboratories described, including also exterior and interior views of the following institutions: Laboraties of the Museum in Paris, of Strasburg University, Bonn University, College of New Jersey, Kent Laboratory of Yale University, University of Michigan, Lehigh University, Cornell University, College of the City of New York, Women's Medical College of the New York Infirmary, and School of Mines, Columbia College.)

## A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

### First Paper: The Analysis of Baric Bromide.

By THEODORE WILLIAM RICHARDS.

(Continued from p. 271).

### *The Method of Analysis.*

Thus far it has been found possible to determine accurately only the ratio of baric bromide to silver and argentic bromide. Unfortunately no accurate method for the direct determination of the amount of metal present is known to exist; hence a complete analysis is impossible.

The usual scheme of operations was very simple. The baric bromide, after having been pulverised in an agate mortar, was heated for a long time at 200—400°; it was then gradually raised to dull redness, and maintained for some time at that temperature. Repeated heating sometimes caused a very slight loss, due to increased decomposition; but more usually the weight remained constant. The drying oven was a large porcelain crucible, and at first illuminating gas was used as the source of heat.

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* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

Afterwards, when a faint trace of cloudiness found in the solution of the baric bromide was traced to the formation of baric sulphate from the sulphur in the illuminating gas, an alcohol lamp was used exclusively. In Analyses 3, 4, 15, 16, and 17, the amount of this insoluble residue was determined, and appropriate correction was made. In Analyses 6, 7, 9, and 12, the cloudiness of the solution was so slight as to be inessential, while in Analyses 2, 5, 8, 10, 11, 14, 18, and 19, the neutral solution of the baric bromide was absolutely clear.

The method of weighing was precisely similar to that employed with anhydrous cupric sulphate (*Proc. Amer. Acad. Arts and Sciences*, xxvi., 243, 252). Afterwards the salt was dissolved in the purest boiled water, and the traces of baric hydrate and carbonate present were determined in the manner which has been already described (see *ante*). The appropriate correction having been applied to the last weight of the baric bromide, the solution was diluted and transferred to a glass-stoppered Erlenmeyer flask. To this was added about the corresponding amount of accurately weighed silver, which had been dissolved in the purest nitric acid with all possible precautions (*Proc. Amer. Acad. Arts and Sciences*, xxv., 198). The argentic nitrate solution had been freed from the lower oxides of nitrogen by long heating at 100° in an inclined flask, and both solutions were quite cold at the moment of precipitation. Daylight was carefully excluded during this operation, as well as during the subsequent ones. After violent shaking, the precipitate was allowed to settle, and the excess of bromine or silver was determined by titration. It is well known that even here there is a slight difference between the end points, although the possible error is very much less than with the chloride. In the Table the mean between the two extremes is recorded; and in general the observations and method of treatment corresponded essentially with those since published for the late J. L. Hoskyns Abrahall in the account of his interesting work on the atomic weight of boron (edited by T. Ewan and P. J. Hartog, *Journ. Chem. Soc. Proc.*, 1892, p. 663), to which the reader is referred. The end point was always determined by titrating backward and forward until there could be no doubt of its accuracy, a c.c. of each of the solutions employed corresponding to one m.grm. of silver. In the final experiments the solutions were weighed as well as measured. For these experiments a dark room was built, and provided with an arrangement essentially similar to that described by Stas (Aronstein's translation, page 45) for condensing a beam of yellow light upon the surface of the liquid in the flask, leaving the precipitate in darkness.

In some cases the baric bromide was poured into the argentic nitrate (*e.g.*, Experiment 14, 15, 16), instead of *vice versa*. This difference of procedure seemed to increase the distance between the two end points, but not to influence the final averaged result (compare Stas, *Mém. Acad. Belg.*, xliii., Introduction).

In most cases a slight excess of hydrobromic acid was added before filtering, but the amount recorded in the Table always represents that which was equivalent to the end point of the reaction. In Experiments 3, 6, 12, 14, and 15, where argentic nitrate was added in excess before filtration, the total amount of silver given in the Table signifies the sum of the amount of silver weighed out and that which was added to attain the end point. The extra silver is, of course, not counted. The agreement of Analyses 14 and 15 with 18 and 19 is sufficient to show the accuracy of both methods. The clear yellow precipitate was washed by decantation until the filtrate became wholly neutral, and was collected and weighed on a Gooch crucible. The first filtrates were always passed through the crucible several times, for fear that a trace of asbestos might have been carried away. One of the absolutely clear filtrates containing a trace of hydrobromic acid gave no sign of a reaction for silver after evaporation to small bulk.

In a number of experiments modifications in the methods described above were introduced. The most important change was the one adopted in Analyses 2, 8, 14, and 18. In these four cases the baric bromide was not heated at all, but the crystallised salt was dissolved directly in water.* In order to determine the amount of anhydrous salt which must have been present in these specimens, parallel determinations of the water of crystallisation were made with the greatest care upon precisely similar samples. The agreement of these results with the others is the best possible proof of the accuracy of the alkalimetric correction applied to those determinations in which the substance had been ignited.

In Experiments 4 and 13 the baric bromide was fused. In Analyses 6, 14, 15, 18, and 19, the argentic bromide was fused, and the weight of the fused salt is recorded in the final Table. In the first case the substance had been slightly darkened by exposure to light; hence a little pure bromine vapour was added to the glass tube in which the fusion was conducted, and the bromide gained 0·07 m.grm. during the process. The other results are tabulated below.

| No. of analysis. | Weight of argentic bromide before fusion. Grms. | Loss of argentic bromide on fusion. Grm. |
|---|---|---|
| 14 .. .. .. | 7·17411 | 0·00018 |
| 15 .. .. .. | 4·4583 | 0·00001 |
| 18 .. .. .. | 3·63751 | 0·00013 |
| 19 .. .. .. | 4·37867 | 0·00000 |

In Experiment 11 a hard glass tube with small rubber stoppers was employed for the ignition of the baric bromide, but it was attacked by the salt and gained 0·10 m.grm. during the heating. This gain corresponds to a loss of about the same weight of bromine, assuming all the barium which combined with the glass to have been converted to the oxide. For this reason the amount of hydrobromic acid recorded in the seventh column of the final Table is about 0·12 c.c. too large. In calculating the corrected weights of baric bromide, silver, and argentic bromide, allowance is made for all these facts. Because of the complication of all these little corrections, the glass tube was abandoned and the platinum crucible was again used.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, May 18th, 1893.*

Dr. Armstrong, President, in the Chair.

Mr. H. A. D. Jowett was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. S. W. M. Davy, Sharrow View, Sharrow, Sheffield; James John Howitt, Dunley, Toft Road, Knutsford; John Walter Leather, 15, Bradgate Road, Catford, S.E.; K. P. McElroy, 1412, Sixteenth Street, Washington, U.S.A.; John Watson Napier, Minto House, Edinburgh; Claude Theodore James Vautin, 10, Hanover Square, London; Edward Augustus Warmington, 266, Castle Street, Dudley.

Of the following papers those marked * were read:—

*20. "*Studies on the Formation of Ozone.*" (II.) By W. A. Shenstone and Martin Priest.

The authors have submitted a known volume of oxygen confined in an ozone generator of the Brodie pattern to

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* This procedure was suggested by a part of Marignac's work on the chloride (*loc. cit.*).

the influence of discharges produced by varying differences of potential, and have determined the amount of ozone produced by observing the change in volume by means of a mercury manometer. A full description is given of the contact breaker used, of the means adopted to measure the differences of potential, to prevent the ozone coming into contact with the mercury, &c.; in some of the experiments the discharge from an induction coil, in others that from an influence machine, was used. The following conclusions are drawn:—

1. It is possible to obtain very fairly concordant results.

2. Provided that the path of the discharge be not too short at any point in the generator, the maximum proportion of ozone that can be produced at a given temperature and pressure is nearly independent of the difference of potential employed, provided that this be between the limits of 33 and 69 C.G.S. (electrostatic) units.

3. If the path of the discharge be very short at any point in the generator, the maximum proportion of ozone that can be obtained has an inverse relation to the differences of potential employed.

4. The rapidity with which oxygen is converted into ozone in a given ozone generator, and under given conditions of temperature and pressure, is greater when great than when small differences of potential are employed, or, in other words, a given percentage of ozone can be obtained more quickly by employing a high difference of potential than by means of a lower one.

5. The maximum proportion of ozone that is obtained in a given generator, at given temperature and pressure, is less when the number of discharges in unit of time is very great than when it is more moderate.

6. The highest proportions of ozone can be obtained (at given temperature and pressure, and if a given difference of potential be employed) by using a generator made of very thin glass and in which the inner tube fits into the outer tube rather closely, but such a generator acts very slowly if the mingling of its contents depend upon diffusion.

7. A greater proportion of oxygen can be converted into ozone in a given generator by means of a given difference of potential, the gas being maintained at a given temperature and pressure, by the action of an induction coil than by means of a "Wimshurst" or "Voss" machine.

The authors conclude from their results that the silent discharge acts by decomposing oxygen molecules into their atoms, which subsequently re-combine to a greater or less extent (according to the temperature and pressure) to form the triatomic molecules of ozone; and that ozone is not formed by the direct action of the discharge.

### Discussion.

Professor McLeod referred to the heating effect of the discharge, and asked whether it had been noticed that a rise of temperature took place in the inner vessel of the generator which might account for the decomposition. He drew attention to the possibility of producing ozone in considerable quantity by subjecting oxygen under pressure to the influence of the discharge in a tube one end of which was at a low temperature: unfortunately the tendency of ozone to explode when in the liquid condition appeared to be a barrier to the successful application of this method.

Professor Ramsay commented on the fact that the authors had paid attention only to the influence of difference of potential, and had not taken into account what was probably of more importance, viz., the quantity of electricity in the discharge.

Mr. Crookes concurred in Professor Ramsay's criticism, and said that perhaps the difference observed in the case of the coil and influence machine might be ascribable to this, as the coil would afford a larger quantity of electricity; and that a rapid discharge would also afford a smaller quantity of electricity than a slow one. Locally the temperature might be very high in such tubes. He then referred to the difficulty he had frequently met with in causing a discharge to pass in "Tesla" tubes: a tube through which no discharge would pass during several minutes would suddenly become luminous, but only when charged dangerously near to the breaking point.

Mr. G. N. Huntley asked whether Mr. Shenstone intended to study the effect of temperature on the yield of ozone; as it was a substance in the formation of which heat was absorbed, its stability should reach a maximum at a temperature fixed by its physical constants, and either above or below this temperature the yield of ozone should fall off. In connection with this, the production of ozone at 1200—1300° C., observed by Troost and Hautefeuille, required confirmation.

The President regretted that no electricians were present to discuss the arrangements adopted by the authors. Professor J. J. Thomson, he knew, held the view that the electric discharge in gases was of the nature of chemical action. Personally he was not satisfied with the evidence adduced by Cundall and Shenstone that only oxygen was concerned in the production of ozone; he was of opinion that it would eventually have to be admitted that the formation of ozone was the outcome of an electrolytic change, in which probably conducting moisture was concerned, somewhat as expressed by the symbols—

$$\begin{matrix} O_2 & OH_2 \\ O_2' & OH_2' \end{matrix} \quad O_2 \begin{matrix} \longleftarrow \\ \longrightarrow \end{matrix} \begin{matrix} O_3 & H_2O \\ O_3' & H_2O^{\cdot} \end{matrix}$$

Mr. Shenstone, in reply, said that the electricity does not flow directly from the induction coil, or machine, into the ozone generator. It acts inductively; the ozone generator being a sort of condenser with a compound dielectric consisting of two layers of glass with a layer of oxygen between them. The discharge inside the ozone generator depends on a surface electrification set up on the glass. The "quantity" of electricity which passes through the oxygen in a given ozone generator at each discharge depends on the difference of potential thus set up, and this in its turn depends on the difference of potential of the inducing charge at the two electrodes of the generator. Therefore when the difference of potential of the inducing charge is increased, the quantity of electricity which takes part in a discharge is increased, and *vice versâ*, and we are in fact studying the effect of different "quantities" of electricity on the gas, and we know when we increase or decrease the quantity.

With regard to the suggestion that the greater "quantity" of the current of a coil may explain some of the phenomena, it would seem that this is not likely to influence the inductive effect of a charge at a given difference of potential. It would simply make it possible to bring up the discharge to the desired difference of potential somewhat more quickly by means of a coil than by means of a machine.

They had not observed any extra heating of the acid in the inner tube of the generator, but rather the contrary. Referring to Mr. Crookes's remarks, he said that they had sometimes observed that the production of ozone did not set in until after some time.

### *21. "*The Relative Strengths or 'Avidities' of some Compounds of Weak Acid Character.*" By John Shields, D.Sc., Ph.D.

The author has calculated the relative strengths of a number of compounds of weak acid character from the rate at which salt solutions hydrolyse ethylic acetate (*Phil. Mag.*, [5], xxxv., 365).

The comparison has been made in decinormal solution, the "dissociation ratio" being taken as the measure of relative strength or "avidity," and in order to obtain a better idea of their relative strengths the compounds examined have been compared with some of the stronger acids taken from Ostwald's tables. The results are contained in the following table, from which it will be seen that in decinormal solution, hydrogen chloride, for example, is about 100,000 times stronger than phenol.

| | |
|---|---|
| Hydrogen chloride | 100 |
| Trichloracetic acid | 68 |
| Dichloracetic ,, | 33 |
| Monochloracetic acid | 4·3 |
| Acetic ,, | 0·35 |
| Biboric ,, | 0·0057 |
| Hydrogen cyanide | 0·0026 |
| Phenol | 0·00094 |
| Carbonic acid | 0·00091 |

*22. "*The Boiling Points of Homologous Compounds. Part I. Simple and Mixed Ethers.*" By James Walker, Ph.D., D.Sc.

The author finds that the boiling points of many homologous series may be expressed by means of the relation $T = aM^b$, where T is the boiling point on the absolute scale, M the molecular weight, and *a* and *b* constants which have values peculiar to each series. He applies the formula to the ethers prepared and investigated by Dobriner (*Annalen*, ccxliii., 1) and Pinette (*Annalen*, ccxliii., 33). The difference between the calculated and observed values is generally considered less than a degree. The following rule is a deduction from the formula:—The logarithm of the ratio of the absolute boiling points of any two members of a homologous series, divided by the logarithm of the ratio of their molecular weights, is constant.

23. "*The Conditions Determinative of Chemical Change.*" By Henry E. Armstrong.

Notwithstanding the large amount of evidence now placed on record that substances commonly supposed to be capable of directly interacting do so only in the presence of at least one other substance, chemists do not appear to have arrived at any clear and consistent understanding of the conditions determinative of chemical change: as each fresh case is recorded, we continue to express surprise, overlooking the fact that Faraday, in his early "Experimental Researches in Electricity," clearly foresaw what the conditions were, and that but a slight extension of his generalisations is needed to frame a comprehensive theory. The subject is of such importance that it appears to me desirable to discuss the bearing of recent observations, especially as they to some extent necessitate the modification of views that I have expressed elsewhere, and in order to attract the attention of physicists, to whom we must now look for guidance in these matters.

Eight years ago, in the course of the discussion on Mr. H. B. Baker's communication on "Combustion in Dried Gases" (*Proc. Chem. Soc.*, 1885, 40), I defined chemical action as *reversed electrolysis*: in other words, in order that chemical action may take place, it is essential that the system operated on comprise an electrolyte. I then pointed out that as neither hydrogen nor oxygen was an electrolyte, a mixture of only these two gases should not be explosive; and, moreover, that as water was not an electrolyte, and it was scarcely probable that water and oxygen or hydrogen would form an electrolyte, it was difficult to understand how the presence of water pure and simple should be of influence in the case of a mixture of hydrogen and oxygen. This forecast has since been verified, the remarkable series of experiments carried out by V. Meyer in conjunction with Krause and Askenasy having clearly demonstrated that the formation of water from hydrogen and oxygen takes place at an irregular rate, and is, therefore, dependent on the presence of a something other than water—I imagine an acid impurity. But this is a consideration which has not yet received the proper attention, and it is, therefore, desirable to emphasise its importance by reference to other cases. Mr. Baker's recent preliminary note on the influence of moisture in promoting chemical action (*Proc. Chem. Soc.*, p. 229) affords several interesting examples:—Thus, he states that neither does hydrogen chloride combine with ammonia nor is nitric oxide oxidised by oxygen if moisture be excluded. In the former case, the addition of water should suffice to determine the combination, as water and hydrogen chloride together form a "composite electrolyte" (*cf. Roy. Soc. Proc.*, 1886, No. 243, p. 268); as neither nitric oxide nor oxygen, however, forms a composite electrolyte with water, in this case water alone should not determine the occurrence of change; but if by the introduction of a trace of "impurity" in addition to water the presence of a composite electrolyte were secured (however high its resistance, owing to the smallness of the amount of "impurity"), action would set in, and when once commenced would proceed at an increasing rate, as nitric acid would be formed and the resistance of the electrolyte would consequently diminish. On this account it will be a task of exceeding difficulty to experimentally demonstrate that nitric oxide and oxygen are inactive in presence of water alone; but there can be no doubt that such must eventually be admitted to be the case, provided always that it is permissible to extrapolate Kohlrausch's observations and to conclude from them that *pure* water is a dielectric. The gradual increase in the rate of change here contemplated corresponds to the period of induction observed by Bunsen and Roscoe in their observations on the interaction of chlorine and hydrogen; the statement recently made by Bodenstein and V. Meyer (*Berichte*, 1893, 1146) that a mixture of chlorine and hydrogen behaves irregularly on exposure to light is a valuable confirmation of Pringsheim's observations, and there is now no room for doubt that *pure* chlorine and hydrogen would be incapable of interacting. That no such irregularity is observed on heating iodine with hydrogen is not surprising, as hydrogen iodide would be formed from the very outset and the electrolyte present would exert a minimum resistance almost at once. There is, however, a significant difference in the behaviour of the two mixtures, as hydrogen chloride should behave as hydrogen iodide, so that the problem is but incompletely solved: it may be that the one mixture was more nearly pure than the other, or it may be that the formation of hydrogen chloride from hydrogen and chlorine, under the influence of light, is dependent on the presence of some particular substance, together with water, and does not take place under the influence of any substance capable of forming a composite electrolyte with water; probably, however, the difference observed is chiefly due to the fact that only one of the actions is reversible under the conditions prevailing in the experiments.

Lastly, attention may be directed to the formation of sulphuric oxide from sulphurous oxide and oxygen, which is readily effected in presence of a catalyst, such as finely divided platinum; it cannot be supposed that the mere presence of platinum would condition the occurrence of change, and doubtless moisture is also necessary, the platinum or other catalyst but serving to promote the oxidation of the sulphurous oxide at a temperature considerably below that at which sulphuric oxide decomposes when heated. The action of surfaces generally may well be of this character, and the converse influence they so frequently exercise is probably an effect of the same order.

I have elsewhere raised the question whether there may not be a difference between actions taking place under the influence of low and of high electromotive forces—whether water, *per se*, may not be an electrolyte towards high, though not towards low, forces in the case of high temperature changes, or those brought about under the influence of the electric spark, for example. More attentive consideration of the subject has led me to think that this is not the case, and that we must treat high temperature changes such as occur and are involved in gaseous explosions in the same way as those occurring under ordinary conditions and at low temperatures. From this point of view, Mr. Baker's statement that ammonia and hydrogen chloride do not combine is of extreme importance; the formation of ammonium chloride from these two compounds apparently involves no interchange, but a mere combination of two substances each endowed with considerable "residual affinity," and there is no reason why a distinction should be drawn between such a case and that afforded by, say, *atoms of hydrogen and oxygen*, the difference being, it would seem, one of degree only: in fact, I am no longer inclined to believe that atoms are capable of directly uniting. In all cases at least one function of the (composite) electrolyte would appear to be that of providing the necessary "mechanism" whereby the degradation or discharge of the energy is effected. If this argument be sound, its logical extension involves the conclusion that *pure* gases should be dielectrics, *i.e.*, that the passage of an electric discharge through a gas like that of an explosive wave through, say, a mixture of hydrogen and oxygen, can only take place if an electrolyte be present. Hitherto but little attention has been paid to the electric discharge in gases which have been highly purified. The peculiar behaviour of Tesla tubes referred to by Mr. Crookes in the discussion on Mr. Shenstone's paper on the formation of ozone is, perhaps, explicable from this point of view—it may be that the atmosphere within the tube does not become conducting until sufficient moisture and "impurity" have been projected from its sides. It is conceivable that a similar explanation may hold good in the case of Professor Schuster's observation, that it is possible to urge a current of low electromotive force across a gas subjected to a high electromotive force in itself insufficient to cause a discharge in the gas; the atomic dissociation hypothesis put forward in explanation of the phenomenon does not appear to me to be sufficient.

Finally, the question arises, Can no line be drawn; are no two pure substances capable of combining or interacting:—For example, water and sulphuric anhydride? There is little to guide us here, but it seems not unlikely that water has special properties which enable it to act directly; moreover—perhaps because—in such cases composite electrolytes would result. Ammonium chloride, so long as it remains solid, is clearly a compound of a different order, and it may well be that compounds of this type are in no case directly obtainable from their constituents, because, under the conditions under which they are formed, they cannot behave as electrolytes.

Apparently, in all cases in which the molecular aggregates are formed—as in the case of solutions—we are dealing with dissociable and dissociating systems, and it is not improbable that we may ultimately find an explanation of the mechanism of such changes in this fact.

At present there is no information forthcoming whether simple electrolytes, such as fused silver chloride, for example, will condition chemical change in the way that water does—whether, for instance, silver chloride will condition the formation of hydrogen chloride from chlorine and hydrogen, so that a gas battery might be constructed of these three substances.

### 24. "*The Nature of Depolarisers.* By HENRY E. ARMSTRONG.

When an electric current is passed between plates of platinum through a solution of sulphuric acid, the hydrogen and oxygen are partly retained at the surfaces—and apparently also within the plates—and under these conditions are capable of interacting, as in the well-known Grove gas battery; so that in so far as the "gases" thus circumstanced are concerned the change may be expressed by a reversible equation. This reversal constitutes the well-known phenomenon termed polarisation by physicists.

Reversal owing to the retention of hydrogen in circuit is promoted to different extents by different metals—hence apparently the varying electromotive forces of single fluid cells containing different negative plates; and when the pressure is sufficient to retain the whole of the hydrogen at the plate, it becomes total—hence it is, for example, that zinc does not dissolve in sulphuric acid under great pressure.

Various substances known generally as depolarisers are used to prevent the accumulation of products of electrolysis and the consequent reversal of the action—such as copper sulphate in the case of the Daniell cell, and "nitric acid" in the case of the Grove and Bunsen cells; but whereas the action of copper sulphate is easy to understand, that of "nitric acid" offers many difficulties. As the heat of dissolution of copper in dilute sulphuric acid is a negative value (about 12,000 units), the displacement of copper by hydrogen, *i.e.*, the heat of dissolution of hydrogen in copper sulphate—is a positive value, so that not only does the presence of the copper sulphate prevent the accumulation of hydrogen, but in removing hydrogen it also serves to increase the electromotive force of the cell from about 37/46ths to about 50/46ths of a volt. The principle underlying this is extensible, even to cases in which one part of the cumulative effect of the cycle of change is a negative value. Thus, although copper has a negative heat of dissolution, it will readily dissolve in dilute sulphuric acid if it be used in place of zinc in a Grove cell, the negative heat of dissolution of copper being more than compensated for by the positive heat of dissolution of hydrogen in "nitric acid"; and it is well known that copper dissolves in many weak acids in presence of oxygen. It is easy to understand how oxygen acts in such cases, but the facts show that the effect produced by "nitric acid" is not so readily interpreted, and their consideration raises important questions of general application.

Russell and Lapraik have shown that when "nitric acid" is freed from nitrous compounds it does not dissolve silver, but that action sets in when a trace of nitric oxide is introduced, and continues with increasing rapidity as the quantity of the nitrous compound—a necessary product of the action—increases; Veley's later experiments have shown that the same is true of copper, without, however, affording any further explanation of the phenomena. Although it is not to be expected that such metals would dissolve in nitric acid even when coupled with a relatively electronegative conductor, as they have negative heats of dissolution, yet if the acid also acted as depolariser a cycle might be formed in which sufficient energy would be developed to condition change; it therefore follows that in such cases nitric acid does not act as the depolariser in accordance with the equation:—

$$2Ag+2NO_3H+ONO_2H=2AgNO_3+H_2O+NO_2H,$$

and that in point of fact the nitrous compound is the depolariser, although the nitric acid is the actual solvent of the metal, the hydrogen of the acid being virtually directly displaced by the metal with the assistance, however, of the current energy derived from its own oxidation by the nitrous compound.

But what interpretation is to be given of the behaviour of more active metals, such as zinc, magnesium, &c., which have positive heats of dissolution, and, therefore, are capable of dissolving in the pure dilute acid if coupled with a relatively negative conductor; does nitric acid in their case directly act as depolariser? If it be capable of thus acting, such metals even when uncoupled should dissolve in the pure diluted acid. It is noteworthy that when such metals are dissolved in nitric acid hydrogen is sometimes evolved. It has been suggested that this hydrogen is derived from the interaction of the metal and water, but I cannot now regard this as as a probable explanation; its production serves rather to suggest a deficiency of the depolarising agent, which cannot well occur if nitric acid be the depolariser. Indeed, if nitric acid be regarded as directly active, it is remarkable that in presence of the large excess of the acid which is always present any hydrogen should escape; and also that the reduction should extend so far as it often does, and not extend merely to the formation of nitrous acid. If, however, the acid be incapable of directly acting as depolariser, and a nitrous compound be the initially active depolarising agent, it is no longer surprising that owing to the nitrous compound suffering further reduction it should be deficient in parts of the circuit, and that consequently hydrogen should escape. Why the reduction should extend so much further when metals having positive heats of dissolution are used, however, still requires elucidation.

In the case of sulphuric acid, whatever metals be dissolved in the *diluted* acid, no reduction takes place; and it is only when the concentrated and more or less heated acid is used that sulphurous oxide and other reduction products are obtained. It appears not improbable that reduction only takes place under conditions under which the presence of sulphuric *oxide* is possible, *i.e.*, that depolarisation is effected by sulphuric *oxide* and never by sulphuric *acid*, although this latter may be regarded as the actual solvent of the metal. There is at present no evidence forthcoming to show that nitric acid can dissociate into the anhydride and water, and even if such a change took place in concentrated solutions, there is no reason to assume that it can also take place in dilute solutions, and that this is the explanation of the difference between nitric and sulphuric acids. It is well known, however, that nitric acid is resolved with extreme facility into nitrogen dioxide, water, and oxygen, and that it is excessively sensitive to the action of nitric oxide—a trace of nitric acid would therefore exercise a fermentative action and condition, the formation, it may be, of nitrous acid, or—as there is no evidence compelling us to suppose that the compound represented by the formula $HNO_2$ exists—it may be of nitrogen dioxide. In this latter case solutions of nitric acid would resemble concentrated sulphuric acid in containing a reducible oxide, and it may be that their depolarising action is initially exerted through such an oxide alone.

To arrive at a clear conception of the function of acids in dissolving metals, and of the nature of depolarising agents, it would, therefore, appear to be necessary to take into account many circumstances to which hitherto but little attention has been paid.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 21, May 23, 1893.

**The Chemistry of the Middle Ages.**—M. Berthelot.—The author has presented to the Academy a new work which he has just completed. The first volume is a study of the Latin alchemy as far as the 14th century. The Syrian alchemy, forming a connecting link between the Greek and the Arabic authors, is considered in the second volume. This volume includes a translation of the great work of Zosimus, the original of which has been lost and which is now known only from a Syrian version. The third volume is devoted to the Arabic authors, especially Djaber (commonly called Geber). The authentic Arabic writings contain little beyond facts already put on record by the Greeks.

**Certain Rare or Novel Natural Phosphates: Brushite, Minervite.**—Armand Gautier.—Brushite is a native crystalline calcium biphosphate, which, as obtained from the Minerva caverns, contains neither chlorine nor fluorine. The minerals in which phosphoric acid is united to aluminium, with or without an excess of base, are variscite, callainite, gibbsite, wavellite, Fischerite, peganite, Evansite, and turquoise. Bauxite often contains an appreciable quantity of aluminium phosphate. Gibbsite may even be confounded with hydrargyllite, which contains no phosphoric acid or a mere trace.

**Determination of Water in Soils Bearing Different Crops After Prolonged Drought.**—M. Reiset.—Wheat may vegetate well and reach perfect maturity in a soil containing only 1·22 grms. water in 100 parts of earth. Grass turf is burnt dead in soils containing 6 8 and 7·84 grms. water per cent.

**Election of a Correspondent for the Section of Physics.**—Herr G. Widemann (Wiedemann?) was elected *vice* the late Dr. Weber by a large majority. Professor Thalén received only 1 vote!

**On Iron Chloroborate and on a Method of Preparing Chloroborates Isomorphous with Boracite.**—G. Rousseau and H. Allaire.—The method followed by the authors consists in causing the vapour of a metallic chloride to react at a red heat upon natural calcium borate or preferably upon boro-sodio calcite. Iron chloroborate crystallises in transparent cubes of a greyish colour, and which act upon polarised light.

**Heat Liberated in the Combination of Bromine with Certain Non-saturated Substances of the Fatty Series.**—W. Louguinine and I. Kablukow.—The authors conclude that the heat liberated in the combination of bromine with the hydrocarbons examined increases as we ascend in the series of the homologues. The presence of an atom of Br replacing H in the non-saturated hydrocarbons retards considerably the speed of the reaction of the addition of bromine. In presence of the group OH the reaction of addition ceases to be definite and is accompanied with a reaction of substitution.

**The Licarhodol Derived from Licareol.**—Ch. Barbier.—The composition of licarhodol is $C_{10}H_{18}O$. It is a colourless, oily liquid, soluble in water, and giving off a strong odour of roses. Under a pressure of 19 m.m. it boils at 122°; its specific gravity at 0° is 0·8952, and in a stratum of 0·20 metre and at a temperature of 20·4° it gives a deflection of $-0° 14'$. On oxidation it yields an aldehyd, $C_{10}H_{16}O_2$.

**Action of Sodium Sulphite on the Salts of the Amidophenols. New Method of Obtaining Amidophenols from the Salts.**—Aug. Lumière and A. Seyewetz.—The authors have succeeded in isolating several amidophenols in a pure state by utilising for the decomposition of their salts a substance with a weak alkaline reaction, the neutral sodium sulphite, which in consequence of its reducing properties prevents the oxidation of the base formed.

**Ptomaine Extracted from the Urine of Patients Suffering from Eczema.**—Dr. A. B. Griffiths.—This base, the extraction of which was described in the *Comptes Rendus*, cxiii., p. 656, is white, crystalline, soluble in water, and of a faintly alkaline reaction. It forms a hydrochlorate, a chloroplatinate, and a chloraurate, all crystalline; it gives a brown precipitate with phosphotungstic acid, yellowish with phosphomolybdic acid, yellow with picric acid, and yellowish with silver nitrate. With mercuric chloride it gives a greenish precipitate. It is also thrown down by Nessler's reagent. The composition of the base is $C_7H_{15}NO$. It is poisonous. A solution of this ptomaine (in sterilised water), if injected under the skin of a rabbit, produces a catarrhal inflammation at the point of injection, a strong fever, and finally death. This ptomaine, which the author names eczemine, is not found in normal urine.

**On $\delta$-Achroglobine: a Respiratory Globuline contained in the Blood of some Mollusca.**—Dr. A. B. Griffiths.—The author has formerly described three colourless globulines which possess the attributes of oxygenation and dis-oxygenation. They are:—$\alpha$-achroglobine in the blood of Patella, $\beta$-achroglobine in the blood of the Chitons, and $\gamma$-achroglobine in the blood of the Tunicata. He has obtained a fourth similar compound from the blood of some species of Doris, and has named it $\delta$-achroglobine. Its analysis leads to the formula $C_{659}H_{792}N_{165}SO_{153}$. It exists in two states, oxidised and reduced. 100 grms. of this respiratory globuline absorb 125 c.c. of oxygen at 0° and under a pressure of 760 m.m. If dissolved in a dilute solution of magnesium sulphate, its specific rotatory power for the ray D is $[\alpha]_D = -54°$. With $CH_4$ it forms a yellowish compound, with $C_2H_2$ a greenish compound, with $C_2H_4$ a brownish compound. These compounds are dissociable in a vacuum.

### *Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 9.

**Synthesis of Erythrite.**—M. Griner.—This paper is the subject matter of a "pli cacheté" deposited with the Society on March 24, and opened on April 14. On saponifying at 100°, by means of baryta water the triacetine obtained from dibromdiacetine, the author has produced a compound which melts at 118° and which presents all the characters of natural erythrite.

**On Certain Substituted Carbides of Benzene.**—P. Genviess.—In this research the author has determined the combustion and formation heats of propylbenzene, isopropylbenzene, normal propyltoluene, and isopropyltoluene. He has established the constitutional formulæ of di-isopropylbenzene, normal propyltoluene, and isopropyltoluene. He has prepared two propylbenzenes monochlorised in the lateral chain, and determined their constitutional formulæ. He has obtained an isopropylbenzene, monochlorised in the nucleus, and seen the position of the chlorine. He has lastly shown that by the action of chlorine in heat it is possible to obtain a propyltoluene chlorised in the lateral chain, and has determined its constitution.

**On Inuline.**—C. Tanret.—The substance hitherto known as inuline is a mixture of two or three substances, the proportions of which differ according to the method of preparation. Its composition approaches—

$$30(C_{12}H_{10}O_{10})5H_2O_2.$$

When air-dried it may be represented as—

$$[6(C_{12}H_{10}O_{10})H_2O_2]5.$$

Over sulphuric acid it loses its water very slowly. Inuline is deposited from its solutions in water in irregular granules of from 0·0005 to 0·002 m.m. in diameter, and from its alcoholic solutions in nearly globular granules, the larger the greater the quantity of alcohol used. With one volume of alcohol they may reach 0·008 m.m., and which have no appreciable action on polarised light. Inuline does not swell up in water. It is very sparingly soluble in cold water (not in 10,000 parts of water at 15° after agitation for several days). It is very soluble in boiling water. In cold dilute alcohol it is insoluble, but dissolves freely with the aid of heat. At 178° it melts, becoming yellow, slightly acid, and very soluble in cold water. At a slightly higher temperature it becomes strongly acid, and is converted into pyroinuline. The specific gravity of inuline dried at 130° is, according to the author, = 1·539, and that of the hydrated compound = 1·478. The rotatory power for inuline dried at 130° is $\alpha_D = -39·5°$. This rotatory power is influenced neither by temperature nor by the concentration of its solutions. Inuline heated with dilute acids does not yield simply levulose, but a mixture of about 12 parts of levulose to 1 part of glucose. Cold baryta water dissolves inuline at first, but a further addition gives a precipitate. Iodine does not colour inuline at all. It does not reduce Fehling's liquid, and has no reaction upon beer-yeast or diastase.

**On Dipropylamidoacetic (Dipropylaminoethanoic) Acid.**—F. Chancel.—The author has prepared this acid, to which he ascribes the composition $C_8H_{17}NO_2$. He has also obtained its compounds with hydrochloric acid, its chloroplatinate, chloraurate, and its copper salt. To the last-mentioned substance he assigns the composition $(C_8H_{16}NO_2)Cu+H_2O$.

**On Acetic Tripropylbetaine (Ethanoyltripropyltaine).**—F. Chancel.—This body is obtained by the action of ethyl monochloracetate upon dry tripropylamine. The author has examined this substance, its hydrochlorate, chloroplatinate, chloraurate, and picrate, as also ethyltripropylaminoethanoate, chloroplatinate, and chloraurate.

**On Dipropylcyanamide and Dipropylcarbodiimide.**—F. Chancel.—The former of these compounds, $C_7H_{14}N_2$, is a mobile liquid of the specific gravity 0·88 at 0°, of a burning taste, and an aromatic odour. It boils at 107° under a pressure of 21 m.m., at 220° under 770 m.m. It is insoluble in water, soluble in alcohol and ether, and does not solidify at −50°. Dipropylcarbodiimide is a mobile liquid of the composition $C_7H_{14}N_2$. It boils at 80° under a pressure of 28 m.m., and at 171° under 765 m.m. It does not solidify at −50°. It is insoluble in water, but soluble in alcohol and ether.

## MISCELLANEOUS.

**The Royal Society and Trade Certificates.**—The subjoined expression of opinion was adopted by the President and Council of the Royal Society at their meeting on May 18, and was ordered to be communicated to all the Fellows of the Royal Society :—

> "The attention of the President and Council of the Royal Society has been called to certain advertisements appearing from time to time in the public newspapers and in various trade journals and circulars, containing certificates and statements signed by Fellows of the Society. These certificates and statements are not in all cases confined to mere analyses or simple matters of fact, but occasionally include expressions of opinion as to the subject matter of the advertisements, and laudatory passages which assume much of the character of an advertiser's encomium. The President and Council fully recognise the liberty of the Fellows to give, when consulted, authoritative statements on chemical analysis or any other scientific facts on which they are called upon to advise. They feel, nevertheless, that in some of the trade certificates already mentioned, due regard has hardly been paid to the status and dignity of the Royal Society, and they are of opinion that the issue of such certificates tends to act injuriously upon the reputation of the Society. They are, however, confident that when attention is called to the subject, all the Fellows will endeavour to express any statements relating to matters of trade or manufacture in such terms that no suspicion of mercenary motives or commercial partisanship can possibly attach to them."

**Photographic Competition.**—We beg to call attention to the advertisement of Messrs. Perken, Son, and Rayment, who are offering prizes for the best sets of photographs taken with their "Optimus" lens.

**Instruction in Dyeing at Aix-la-Chapelle.**—With the commencement of the winter term a new special school for dyeing will be opened in connection with the local polytechnicum. All the appliances will be adapted to the most recent advances in the tinctorial art.—*Chemiker Zeitung.*

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, ur such trade notices as should legitimately come in the advertisement columns.

Grinding and Polishing Quartz.—(Reply to "Amateur.")—Formerly quartz was cut on a lead wheel with emery and water, and polished on a zinc wheel with putty of tin and water. This process may perhaps suit your correspondent.—Wm. Brown, 14, Dale Street, Liverpool.

## MEETINGS FOR THE WEEK.

Wednesday, 21st.—Geological, 8.
—— Meteorological, 7.
—— Microscopical, 8.
Thursday, 22nd.—Royal Society Club, 6.30. (Anniversary).
Friday, 23rd.—Physical, 6. Exhibition of a Form of Carey-Foster Bridge, by Mr. Nalder. An Influence Machine, by Mr. Pidgeon. An Influence Machine, by Mr. Wimshurst. A New Volumenometer, by Mr. Myers.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1752.

## ON THE METALLURGY OF LEAD.*

By J. B. HANNAY, F.R.S.E., F.I.C.

In this paper the author details the results of seven years' researches on the metallurgy of lead.

It was found that all the information given in the chemical authorities was erroneous, and every point had to be made the subject of a special study.

The subject is divided into the following sections:—

1. The relations of lead and sulphur.
2. Specific gravity of sulphide of lead.
3. Methods of analysis.
4. Furnace reactions of lead compounds.
5. Lead smelting.
6. New metallurgy of lead.

It is shown that all mixtures of lead and its sulphide, or what may be called subsulphurised lead, can be fractionated into the two extreme terms, metallic lead and its monosulphide, by simply melting and crystallising out the higher sulphurised portion, as the sulphur tends to form monosulphide, which crystallises out and leaves a lead poorer in sulphur as the "mother liquor." This process may be carried on till pure metallic lead is left.

It is then shown that the accepted specific gravity of sulphide of lead is too low, as it oxidises when pulverised and boiled with water, and instead of being 7·585, it is 7·766, and a curve is constructed of the specific gravities of all sulphurised compounds of lead from PbS to Pb.

The methods of analysis are examined, and shown to be fallacious, and a more reliable method devised.

The formula given for the reaction going on in the reverberatory furnace when lead is smelted, viz.:—

$$PbS + PbSO_4 = 2Pb + 2SO_2,$$

is shown to have no existence in fact, as when sulphide and sulphate of lead act upon each other a volatile compound $PbS_2O_2$ is formed, which introduces complications, and the reaction takes a different direction. The discovery of this compound supplies the explanation of the question, "Why does galena form a fume in the air when it is absolutely fixed in nitrogen and hydrogen?"

A series of volatile compounds of one molecule of PbS with a molecule of $CO_2$, $H_2O$, $SO_2$, and CO, is shown to exist.

These compounds are unique amongst combinations between solids and gases, as they are only stable at a red heat and dissociate on cooling, which is the reverse of the behaviour common to such compounds.

All the reactions involved in furnace reactions of lead, its oxide, sulphate, and sulphide, are then traced from their beginning to the final products, as well as the reaction of sulphate and silicate with carbon, and the decomposition of sulphite of lead by heat. The knowledge so gained is applied to lead smelting, and this is shown to be really a fractionation of a low sulphide into lead and its sulphide accompanied by rapid oxidation with the formation of an oxysulphide PbS.PbO, which is the basis of black and grey slags. The operations involved in smelting are shown to be explainable by the new reactions discovered, and Percy's remark that the chemistry of lead smelting was still unexplained is shown to be no longer appplicable.

It is pointed out that the new knowledge enables us to map out a new metallurgy of lead, by which we are enabled to avoid the formation of the oxysulphide which forms slag, and to turn the troublesome volatile oxysulphide, which forms fume, to useful account. The silver can be eliminated, and any proportion of lead, its sulphate, or oxide, formed direct from galena.

Some of the curious crystalline forms of lead sulphide which have been observed during these researches are shown, one of which illustrates very clearly the fractionation of a low sulphide into lead and the monosulphide.

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* Abstract of a Paper read before the Royal Society.

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## BLACK VARIETY OF ANTIMONY TRISULPHIDE.

By C. A. MITCHELL, B.A. (Oxon).

The following quick method of preparing the black variety of $Sb_2S_3$ may be found useful as a lecture experiment:—

About 5 grms. of $Sb_2O_3$ are dissolved in about 30 c.c. of HCl (two parts of acid to one of $H_2O$), and $H_2S$ passed in to saturation. The liquid with the orange sulphide in suspension is then kept boiling over a Bunsen, while a current of $CO_2$ is passed through. In the course of a few minutes a good deal of the orange precipitate dissolves, while some falls down as the black sulphide. By again passing $H_2S$ through the liquid and repeating the above process, more may be converted into the black variety, and by continued repetition the whole may be thus transformed in a short time.

Analysis of this black sulphide shows a percentage of antimony corresponding to that required by the formula $Sb_2S_3$.

King's College Laboratory.

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## THE FLASH-POINT AND POINT OF DANGER IN MINERAL OILS.

By D. R. STEUART, F.I.C., F.C.S.

The danger of fire or explosion from a mineral oil is tested by taking its flash-point. The Government test of Professor Abel is a 2-inch cup covered on the top. The filling, heating, light applied, &c., are all defined. Holes are opened in the lid for a moment to apply the light at specified intervals, and the point got is very definite. The question is: What relation has the point so got to the point of danger? Is the Abel flash-point itself the point of danger, or is danger to be feared only at a much higher temperature?

Before a Parliamentary Committee some years ago, a witness said there was no danger at all until the temperature of the American fire test. The flash-point is the lowest temperature at which the vapours and air give a little explosion when the light is applied, going instantly out. The fire-point is the lowest temperature at which the vapours burn continuously.

A particular sample of oil I tested flashed in Abel test at 78° F., in the old Government open test at 105°, and fired in the old Government open test apparatus at 122°. This last is something like the American fire test. Is there, with this oil, no danger of fire in a store or explosion in a lamp until about 120° F. is reached?

A moment's thought will satisfy us that although a little cup of oil cannot supply sufficient vapour to keep up a constant flame until 122° F. is reached, a larger surface will supply vapour, and, when ignited, heat, enough to produce a constant flame at a much lower temperature. I tried the oil mentioned above in an apparatus like the old Government open test, with screen around and partly also on the top, but 9 inches in diameter. Applying a small flame every two degrees at a half-inch above the surface, the oil ignited explosively at 88°, and continued to burn furiously. Repeating the experiment, and applying the flame at every degree, it ignited and burned continuously at 87°, and the flame rapidly increased in vigour. Making the same apparatus a close test like Abel's, the oil ignited and fired (burned continuously) at 76° F.; that is with a 9 inch wide closed test, instead of the 2 inch prescribed by act of Parliament, the oil not only flashed but fired two degrees below the flash point Abel test, and when open it fired only nine degrees above the Abel test. With a wider surface of oil, the flashing and firing would no doubt take place at even a lower temperature. These experiments prove, if they require proving at this time of day, that the old Government open test and the American fire test are altogether deceptive, and that in store, barrel, or tin can, the flash-point Abel test is a point of real danger, and that for oil in large masses the danger begins even below the flash point (Abel). The experiments also prove that, except for very small surfaces of oil, the flash-point and the fire-point are the same.

The following happened in my experience:—

A large tank of very high flashing oil was being pumped into, and the oil therefore in considerable commotion. The temperature was far below the flash-point in Abel cup; nevertheless, vapours were evolved and filled the top of the tank, and, expelled by the rising oil, overflowed out at a manhole door on the top which was not quite close, and ignited at a lamp some distance below. The fire ran up the stream of vapour; there was an explosion, blowing off the top of the tank, and the oil caught fire and burned uncontrollably until it was practically all consumed. For danger in oil works, even the Abel flash-point is deceptively high. Is it because this has not been realised that fires in oil works have been so frequent?

In regard to danger in a lamp, in 1872 before a Select Parliamentary Committee, a chemical expert said:—"We have made a great number of experiments to ascertain whether oils which flash at 100° (equivalent to 73° Abel test) or even a little below 100°, can by any contrivance be exploded in a lamp, and we cannot do it; whether by electric spark or by flame of any kind, but we cannot fire it; that we have ascertained to be a fact." Now the real fact is that a lamp filled with oil of 100° old open test, if shaken up—as by carrying the lamp—can be exploded with electric spark quite easily, even at 73°. The explosion is not violent; but at 5° above the flash-point (Abel) the explosion may be very violent. Such an oil can explode violently at any temperature between 78° and 120°; that is, at all temperatures lamps are generally exposed to. For lamps burning heat up the oil, more with large lamps than with small, more with metal lamps than with porcelain, more if with metal safety tubes than without, and more with flat burners than with central draught. As all ordinary lamps are more than two inches wide, the flash-point in them will be the Abel flash-point or a little lower. There is a little danger even at the Abel flash-point, for although the explosion at that temperature is a mere puff, yet if it happened while the lamp was being carried it might cause it to be thrown down on combustible material. At any rate, at five degrees above the Abel flash-point the danger is very great.

I have tried many experiments oversetting cheap glass lamps when burning so as to break them. I had the lamp half filled with oil and heated to certain definite temperatures. At 5° above the flash-point (Abel) all in general went out. At 10° above flash-point with some low flashing (73° to 78°), petroleum ignited and burned vigorously, and some merely flashed and went out. High flashing oils (100° to 110° Abel), 10° above flash point invariably went out or merely flashed; they never permanently ignited. At 15° above the flash-point the high flashing oils inflamed, but burned quietly, and the fire could easily have been commanded. So low flashing oils may be a great danger if overset at 10° above flash-point; but high flashing oils are not in great danger until 15° over flash-point or more; that is, if overset on an ordinary floor. If overset on easily combustible materials, there is great danger, even at the flash-point, and as the absence of combustible materials cannot be depended on, even for this kind of accident, the flash-point (Abel) becomes the point of danger. If an open cup of oil heated to the flash-point (Abel) has a large lighted candle plunged into it, the candle is extinguished just as by water. These experiments show the freedom from danger in lamp, or in any small quantities, and particularly of high flashing oil, if kept several degrees under the Abel flash-point.

High flashing oils burn practically as coolly as low flashing oils, and if we seek safety by using a high flashing oil we are not running into any other danger.

Coroner's inquests are very frequent on lamp accidents. It has become the custom for the inspectors to state that no dangerous oil is now imported into England, and inspector and coroner put the whole blame on the lamp. But surely no scientific man is free to state that 73° flashing oil is safe in our climate. It is often 80° or over it in houses, and all the year round the temperature in ordinary lamps is 80° to 90°. The danger is not a mere matter of opinion, but an easily ascertainable scientific fact; and when a scientific man makes such a statement regarding a matter involving hundreds of deaths in England every year, I think he should somehow be amenable to the ban of the profession, if to nothing else. It is absurd to condemn the poor for not having safety lamps; besides, even if they had them, they are only an extra source of danger unless in proper order, and with cheap lamps and ignorant people that could not be depended on.

It is obvious to common sense that the poor should be supplied with oil, such as the rich supply themselves with, safe to work with at ordinary temperatures, and perfectly safe from danger of explosion in ordinary lamps properly attended to. With ordinary petroleum there are many real lamp explosions, in spite of all that is said to the contrary. Carry the lamp about, attempt to blow it out, or turn down the wick too far, and the lamp explodes. These could never happen with an oil whose flash is a few degrees above the temperature of the oil in the lamp. Lamp fatalities are so dreadful that one would think that a few would waken up the people so as to get the matter put right; but the deadly tale goes on day by day, but it is among the very poor, and nobody seems to care. The Government, contrary to the example of all other civilised countries, has given what is practically a certificate of safety for oils flashing above 73°, and, instead of protecting us, has, by legislation, shut itself out from the power of interfering. So these dangerous oils can be stored in any quantity anywhere. Store proprietors and railway companies exercise great care; nevertheless, our lives are at the mercy of the idiosyncracy of individuals, and we may expect a catastrophe on the grand scale some day.

In the past, nobody took any interest in the petroleum laws except the representatives of the oil trade. It is time scientific men, for the sake of the voiceless poor, should pay some attention to the matter. The science put before the Parliamentary Committee was sometimes of a strange kind, and matters of fact were treated as matters of opinion instead of being settled by experiment. It is evident the Government does not know that the flash-point (Abel) is in all cases a point of real danger, and in stores and tanks of great danger. They evidently think there is no danger until the temperature of the old open test. They would never have lowered the safety-point from 100° to 73° if they had known that the old test was deceptive by that interval—and they ought to have known.

Oil vapours when hot, as in the old open test, diffuse away pretty rapidly, but when cold, as in a store, they are very heavy, roll along to the lowest point, and if there are no air currents diffuse away very slowly. They can be decanted from vessel to vessel like carbonic acid gas; but this the Government officials are ignorant of, and think that oil vapours diffuse rapidly into the atmosphere like coal gas.

A little attention by scientific men to our petroleum laws would even cause them to be altered so as to do away with our present horrors and terrors. The development of this great trade on safe lines, in conformity with physical and moral law, would bring a great and immediate blessing to the people, and very soon a great advantage to manufacturers and the trade.

## THE EXAMINATION OF PAPER FOR METALLIC PARTICLES.

By **CLAYTON BEADLE.**

Paper frequently contains particles of impurities that are difficult to identify even under the microscope. They are frequently metallic iron derived from the iron tanks, beaters, &c., in which the pulp has been treated, and brass derived from the wearing down of the beater bars, and, in the case of rag-papers, from the buttons.

The presence of these metallic particles is often the means of spoiling large quantities of paper, and a ready means of their detection is to be welcomed by paper-makers. The following I have found of great service:—

Strips of the suspected paper are floated in a 1 per cent solution of potassium ferrocyanide acidified with a few drops of nitric acid. After three hours' treatment, particles of iron will be rendered evident by the production of deep blue spots, and brass by chocolate-coloured spots. The former are very satisfactory, but the latter may easily be mistaken for other foreign matter contained in the paper.

To confirm the presence of brass particles I place a bead of silver nitrate solution on the suspected spots, and examine them under the microscope by reflected light. If any brass is present clusters of crystals of metallic silver will soon be seen forming themselves on the surface of the paper. After the solution has nearly dried into the paper, a drop of potassium ferrocyanide solution is placed close to the margin. On diffusion it produces a chocolate colouration about the margin. Other metallic particles are seldom met with.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending May 31st, 1893.

By **WILLIAM CROOKES, F.R.S.,**
and
**WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,**
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, June 7th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The character of the water supply to the metropolis during the month of May continued to be in all respects entirely satisfactory. The proportion of organic matter present, as indicated by the estimations of organic carbon, of oxygen required for oxidation, and of the colour tint of the water, was exceedingly minute, the mean results of these estimations, in the case for example of the Thames-derived samples, being identical with those afforded by the previous month's supply already commented on for their exceptional lowness, as shown in the following Table:—

| 1893. | Ratio of brown to blue tint. | Oxygen required for oxidation. | Organic carbon per 100,000. | Organic carbon per 100,000. |
|---|---|---|---|---|
| | Means. | Means. | Means. | Maxima. |
| April .. .. | 11·9 : 20 | 0·28 | 0·088 | 0·125 |
| May .. .. | 11·3 : 20 | 0·29 | 0·089 | 0·124 |

No appreciable difference was noticeable in respect to the proportion of common salt, about one and a half grain per gallon, present in the water in flood time and during the present dry period; but, as shown in the following Table of Thames water results, the proportions of oxidised nitrogen and the degree of hardness underwent during the later months, probably from the increasing activity of fluviatile vegetation, a steady and appreciable decrease.

| 1893. | Common salt per 100,000. | Nitric acid per 100,000. | Degrees of hardness per gallon. |
|---|---|---|---|
| February .. .. | 2·242 | 0·952 | 17·56 |
| March.. .. .. | 2·167 | 0·931 | 16·80 |
| April .. .. .. | 2·181 | 0·888 | 15·11 |
| May .. .. .. | 2·196 | 0·611 | 14·66 |

All of the 182 samples examined during the month were found to be clear, bright, and efficiently filtered.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## A REVISION OF THE ATOMIC WEIGHT OF BARIUM.*

### First Paper: The Analysis of Baric Bromide.

By **THEODORE WILLIAM RICHARDS.**

(Concluded from p. 284).

### *Data and Results.*

The first column of the final Table of Data gives the number of the experiment. The second column contains the weight of the crystallised baric bromide, while the third contains the observed weight of the ignited baric bromide. After this is recorded the number of c.c. of standard hydrobromic acid (of which one litre corresponded to a grm. of silver) required to restore the small amount of bromine lost during ignition. This quantity is divided into two parts, the upper one corresponding to baric hydroxide, and the lower to baric carbonate. Multiplying the upper figure in this column by $\frac{63}{108}$ m.grm., and the lower figure by $\frac{50}{108}$ m.grm., and adding the two products to the weight given in column III., we obtain the corrected weight of the baric bromide, which is recorded in the fifth column. The sixth column gives the total weight of silver taken; the seventh, the number of c.c. of the same hydrobromic acid necessary to titrate back to the mean end point; and the eighth, the weight

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* *Proceedings of the American Academy of Arts and Sciences*, vol. xxviii.

TABLE OF DATA.—(All weights are corrected to the Vacuum Standard).

| I. No. of Analysis. | II. Weight of Crystallised Baric Bromide. | III. Observed Wt. of Anhydrous Baric Bromide. | IV. HBr solution to Neutral Alkali. | V. Corrected Wt. of Anhydrous Baric Bromide. | VI. Total Weight of Silver. | VII. HBr solution to titrate back. | VIII. Weight of Silver corresponding to $BaBr_2$. | IX. Total Weight of Argentic Bromide. | X. Argentic Bromide corresponding to $BaBr_2$. | XI. Sample of Baric Bromide used. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Grms. | Grms. | C.m.³ | Grms. | Grms. | C.m.³ | Grms. | Grms. | Grms. | |
| 1 | 2·56714 | 2·28760 | — | — | 1·66314 | 2·40 | 1·66074 | 2·89444 | 2·89026 | I.*a* |
| 2 | 3·89534 | Not ignited. | 0 | 3·4712 | 2·52554 | 5·35 | 2·52019 | 4·39566 | 4·38635 | I.*a* |
| 3 | — | 3·80860* | 1·90<br>2·50 | 3·81086 | — | 0·30 | — | 4·81740 | 4·81688 | I.*b* |
| 4 | — | 2·19830* | 1·65<br>0·25 | 2·1994 | 1·59832 | 1·45 | 1·59687 | — | — | I.*b* |
| 5 | — | 2·35954 | 0·12<br>0·22 | 2·35971 | 1·71613 | 2·90 | 1·71323 | 2·98735 | 2·98230 | I.*c* |
| 6 | 3·30433 | 2·94178 | 0·32<br>0·22 | 2·94207 | 2·13889 | 3·05 | 2·13584 | 3·72340 | 3·71809 | II.*a* |
| 7 | 1·80930 | 1·61177 | 0·16<br>0·11 | 1·61191 | 1·17100 | 0·80 | 1·17020 | — | — | II.*b* |
| 8 | 2·36427 | Not ignited | 0·00 | 2·10633 | 1·53056 | 1·35 | 1·52921 | 2·66426 | 2·66191 | II.*b* |
| 9 | — | 2·91650 | 0·32<br>0·26 | 2·91682 | 2·11840 | 1·00 | 2·11740 | 3·68789 | 3·68615 | II.*c* |
| 10 | 2·66363 | 2·37226 | 0·38<br>0·90 | 2·37290 | 1·72298 | 0·22 | 1·72276 | 2·99906 | 2·96868 | III. |
| 11 | 2·07483 | 1·84804 | 0·14<br>0·00 | 1·84822† | 1·34328 | 1·65† | 1·34175† | 2·33797 | 2·33530† | III. |
| 12 | — | 1·9038 | 1·40<br>0·00 | 1·9046 | — | 0·37 | — | 2·40798 | 2·40733 | IV.*b* |
| 13 | 2·75591 | 2·45417 | 3·06<br>0·30 | 2·45611 | — | — | — | — | — | IV.*a* |
| 14 | 6·35791 | Not ignited | 0·00 | 5·66647 | 4·12090 | 7·30 | 4·11360 | 7·1739 | 7·1612 | IV.*a* |
| 15 | 3·95705* | 3·52610* | 0·35<br>0·85 | 3·5267 | 2·56100 | 0·90 | 2·56010 | 4·4583 | 4·4567 | IV.*a* |
| 16 | 4·8442* | 4·3161* | 0·00<br>1·75 | 4·3169 | 3·13550 | 1·20 | 3·13430 | — | — | V. |
| 17 | 3·78040* | 3·36557* | 0·15<br>1·50 | 3·36635 | 2·44567 | 1·82 | 2·44385 | — | — | VI.*b* |
| 18 | 3·22971 | Not ignited | 0·00 | 2.87743 | — | 0·54 | — | 3·63738 | 3·63644 | VI.*a* |
| 19 | 3·88750 | 3·46330 | 0·03<br>0·32 | 3·46347 | 2·51529 | 1·14 | 2 51415 | 4·37867 | 4·37669 | VI.*a* |

* Corrected for small amount of baric sulphate (or silica) found on solution.

† See *ante*, p. 284.

N.B.—Two weights (the argentic bromide of Analysis 4 and the silver of Analysis 18) are omitted from this Table, as they were known to be in error. It might have been well to omit the whole of the twelfth experiment for the same reason. The other blanks were never filled.

of the silver corrected by subtracting from the weight given in column VI. the amount of silver corresponding to the quantity of acid given in column VII. In the same way, the ninth and tenth columns contain respectively the total and the corrected weight of argentic bromide. Hence the weights actually used in the calculation of the results are those recorded in columns V., VIII., and X.

The discussion of the results is simplified by reducing all the amounts of baric bromide to the basis of 100·000 parts of silver, and the corresponding quantity, 174·080 parts, of argentic bromide. The water of crystallisation is included in the following Table only because the calculation of Analyses 2, 8, 14, and 18 depends upon the knowledge of its amount. The great variations noticeable in the results for the water of crystallisation are due to the varying circumstances attendant upon the crystallisation, to the fineness of the powder, and to the hygroscopic condition of the air at the time of weighing the crystals. Hence for the present purpose it was possible to compare only like samples which had been weighed out under like conditions. Analyses 13 and 15 show that in this way perfect constancy can be reached. This part of the work has of course no other bearing upon the atomic weight of barium.

The first two experiments were merely preliminary, and are not included in the final average. Most of the variations evident in the earlier experiments were undoubtedly due to unfavourable conditions existing in the laboratory during the year 1891—92. In the autumn of the latter year the laboratory was completely and most admirably remodelled, through the kindness of the Corporation of the University, and the last seven experiments were performed under conditions as favourable as could be desired.

The presence of any of the most likely metallic impurities — strontium, calcium, potassium, or sodium— would tend to lower the observed values recorded in the third and fourth columns of the Table of Results, and hence the atomic weight of barium. Chlorine would lower and iodine would raise the values given in the third column, but neither would have much effect on those given in the fourth column. The best possible proof of the freedom of the preparations from these two impurities, as well as of the purity of the silver, is to be found in the

TABLE OF RESULTS.

| No. of Anal. | Salt employed. | Parts of Baric Bromide corresponding to 100·000 parts Silver. | Parts of Baric Bromide corresponding to 174·080 parts Argentic Bromide. | P.c. of Silver in AgBr. | Water of cryst. in Baric Bromide. |
|---|---|---|---|---|---|
| 1 | I.*a* | 137·746 | 137·783 | 57·460 | 10·889 |
| 2 | I.*a* | 137·736 | 137·760 | 57·455 | |
| 3 | I.*b* | | 137·723 | | |
| 4 | I.*b* | 137·732 | | | |
| 5 | I.*c* | 137·735 | 137·739 | 57·447 | |
| 6 | II.*a* | 137·748 | 137·748 | 57·445 | 10·964 |
| 7 | II.*b* | 137·747 | | | 10·910 |
| 8 | II.*b* | 137·740 | 137·747 | 57·448 | |
| 9 | II.*c* | 137·755 | 137·748 | 57·442 | |
| 10 | III. | 137·738 | 137·752 | 57·451 | 10·915 |
| 11 | III. | 137·747 | 137·772 | 57·455 | 10·922 |
| 12 | IV.*b* | | 137·726 | | |
| 13 | IV.*a* | | | | 10·878 |
| 14 | IV.*a* | 137 750 | 137·745 | 57·443 | |
| 15 | IV.*a* | 137·756 | 137·754 | 57·445 | 10·875 |
| 16 | V. | 137·731 | | | 10·885 |
| 17 | VI.*b* | 137·748 | | | 10·953 |
| 18 | VI.*a* | | 137·745 | | |
| 19 | VI.*a* | 137·759 | 137·758 | 57·445 | |
| Aver., omitting Exps. 1 and 2 .. | | 137·745 | 137·747 | 57 448 | |
| Average of last seven Expts. .. | | 137·749 | 137·751 | 57·444 | |
| | | Stas found .. .. .. .. | | 57·445 | |

series of results giving the per cent of silver in silver bromide, tabulated in the fifth column of the Table of Results (*Proc. Amer. Acad. Arts and Sciences*, xxv., 212). The presence of water in the ignited baric bromide would naturally tend to raise the figures given in both the third and fourth columns; the arguments indicating the absence of this insidious impurity were discussed at length in the first part of the paper (see *ante*).

The agreement between the individual results is as close as could reasonably be expected, when one considers the small amounts of material used in some cases. It may be concluded, then, that a hundred parts of silver correspond to about 137,747 parts of anhydrous baric bromide, no matter what may be the method used for its preparation. If the salt contains an impurity, it is strangely constant in amount.

### *The Atomic Weight of Barium.*

From the results which have just been given, the atomic weight of barium is very readily computed. In the following Table are given the values corresponding to the three standards at present in use.

*From the Ratio of Silver to Baric Bromide.*

If silver = 107·93, and bromine = 79·955, barium = 137·426
If silver = 107·66, and bromine = 79·755, barium = 137·083
If silver = 107·12, (oxygen = 15·88), barium = 136·396

Greatest variations from the mean, $\left\{\begin{array}{l}+0\cdot030.\\-0\cdot040.\end{array}\right.$

*From the Ratio of Argentic Bromide to Baric Bromide.*

If argentic bromide = 187·885, barium = 137·431
If argentic bromide = 187·415, barium = 137·089
If argentic bromide = 186·476, barium = 136·401

Greatest variation from the mean, ± 0·054.

It is not very difficult to explain the reason for the difference between this new value, 137·43, and the old one, 137·10. The incomplete knowledge regarding the end point of chlorine reaction in 1858 is probably responsible for a part of the difference, and a portion more may possibly be explained by the impurities which were assumed to be inessential. But it has already been said that a discussion of the results of thirty-five years ago can be of little value. The only true solution of the question is the experimental one. In the near future I hope to continue the investigation which is herewith commenced, as well as to begin a similar research upon strontium and calcium.

## THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Continued from p. 261).

### *Manganese.*

Two grms. of the sample, contained in a beaker, are treated with 50 c.c. of nitro-hydrochloric acid, and gently heated until the iron has dissolved. The solution thus obtained is transferred without loss to a flask of 2½ litres capacity, diluted with water until the volume occupied measures 1½ litres, and heated to nearly a boiling temperature. The next step is to precipitate the iron existing in the solution as ferric chloride, which is accomplished by cautiously adding ammonia (sp. gr. 0·88) until it remains slightly turbid, after well agitating the containing vessel. Instead of employing ammonia throughout, it is advisable, as the solution approaches neutrality, to substitute for it a dilute solution, about 1 part in 20 of water. To the slightly turbid liquid add 250 c.c. of hot ammonium acetate, bring it to boiling point, and allow it to stand until the brick-red precipitate of basic acetate of iron has settled. Pass the solution, together with the precipitate, on to a large English filter-paper, and thoroughly wash with hot water containing a little ammonium acetate.† Sometimes, owing to the incomplete precipitation of the iron, a perfectly clear filtrate is not always obtained. This, however, is rather to be desired than otherwise, as the probability of the iron carrying down with it small portions of the manganese is much less than where the precipitation is complete. Should such be the operator's experience, the filtrate is heated to boiling for five minutes, when upon re-filtering it will be found to run through clear.

To facilitate the precipitation of the small quantity of manganese contained in the bulky filtrate, it is concentrated by evaporation until it occupies a volume of 400 c.c. The concentrated solution is now thoroughly cooled, and when this is effected bromine is added until it is of a dark brown colour. This reagent is added in small quantities at a time, and the containing vessel well agitated with each addition. To this brown coloured solution strong ammonia (sp. gr. 0·88) is added until strongly ammoniacal, when it is heated to boiling, and the resulting precipitate of hydrated peroxide of manganese collected on a filter, well washed with water, converted by strong long-continued ignition at a high temperature into tri-manganic tetraoxide, $Mn_3O_4$, every

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* From *Industries*.

† The details of the method as here given must be strictly adhered to.

hundred parts of which are equivalent to 72·05 per cent manganese, and weighed. The manganese precipitate often contains a small quantity of iron, and as its presence would impair the accuracy of the determination, it becomes necessary to test the $Mn_3O_4$, after weighing, for the metal, and if any be found, the amount determined and deducted from the weight of the precipitate. With this object, dissolve the $Mn_3O_4$ in a small quantity of hydrochloric acid, withdraw a drop of the solution on the end of a glass rod and bring in contact with a drop of sulphocyanide of potash spread on a white porcelain slab. A pink colouration is formed varying in intensity in proportion to the amount of iron, if any, present.

Two methods, either gravimetric or colorimetric, may be employed for the quantitative determination of the iron; of the two, the latter is preferable. In using the gravimetric method, the hydrochloric acid solution of the $Mn_3O_4$ precipitate is diluted with six times its bulk of water, made neutral with ammonia, and the iron thrown down by the addition of a small quantity of hot ammonium acetate; the solution is boiled, the precipitated basic acetate of iron collected on a filter, washed, converted by ignition into ferric oxide, $Fe_2O_3$, and weighed, which weight is deducted from that of the $Mn_3O_4$. If Parry's colorimetric method is employed, the manganese precipitate, &c., is dissolved in nitric acid with a few drops of hydrochloric acid. The solution is then transferred to a Nessler's cylinder, four drops of a weak solution of sulphocyanide of potassium added, and cold water is afterwards added until the volume occupied measures 50 c.c., and thoroughly mixed. The colour of this solution is now compared with that produced by taking various quantities of a solution containing a known quantity of iron, adding four drops of sulphocyanide of potassium, and making up with water to a volume occupying 50 c.c., until equality of tints is arrived at. The iron, equal to the number of c.c. of the "standard" solution required, is calculated into ferric oxide, $Fe_2O_3$, by multiplying by 1·429 and deducted from the weight of the $Mn_3O_4$ precipitate. The "standard" solution of iron is prepared of such a strength that a litre contains one grm. of the metal. A steel of known composition may be employed; assuming that it contains 99·5 per cent of iron, a solution containing one grm. of iron is obtained by dissolving 1·005 grms. in a small quantity of $HNO_3$ (1·20 sp. gr.) and diluting to a litre. This colour test is also used for the determination of small quantities of iron in blast furnace slags, &c.

Iron is not the only metal which may be contained in the manganese precipitate, as copper or nickel present in the iron or steel would be partly thrown down with it. Its removal may be effected either in the original acid solution of the metal or from the $Mn_3O_4$ precipitate after weighing. The separation of the copper, &c., in the original solution of the iron or steel will be described under the determination of that metal.

Under certain conditions, potassium chlorate precipitates manganese as black peroxide from a nitric acid solution of the iron and steel. This forms the principle of a method—a combination of the bromine and potassium chlorate method—which furnishes very good results in a much shorter time than the one just described, and allows of a larger quantity of the metal being operated upon. For analysis, 4 grms. of the sample contained in a conical or small flask are digested with 60 c.c. of nitric acid (sp. gr. 1·20) at a gentle heat until the whole is dissolved, when 30 c.c. of nitric acid (1·42 sp. gr.) are added. This solution is heated to boiling, and while at this temperature 6 grms. of potassium chlorate added, a few crystals at a time. After boiling for a period of fifteen minutes, a further addition of the same quantities of acid and potassium chlorate is made, and the solution again brought to, and kept at, boiling temperature for the same period. The solution is now thoroughly cooled, diluted with cold water, and allowed to stand until the precipitated black oxide of manganese, containing also a little iron, has completely settled, when the supernatant liquid is passed through a Swedish filter without throwing on the precipitate. The small quantity of the manganese oxide which has accidentally passed on to the filter is dissolved in hydrochloric acid, receiving the solution in the vessel containing the bulk of the precipitate, which is also dissolved by the addition of a further quantity of acid and the application of a gentle heat. The resulting solution is now diluted with 200 c.c. of water, the iron carefully precipitated as basic acetate, with ammonia and ammonium acetate, separated by filtration, and the manganese contained in the filtrate precipitated with bromine as previously described. We find this method preferable, for practical, work, to that given by M. Troilus, in which the manganese peroxide precipitate is carefully washed until free from iron, and the manganese determined either by direct weighing or a volumetric method.

Spiegel and ferro-manganese may be very well done by the acetate method, or by the volumetric determination of the iron, allowing 6·0 for spiegel, and 7 to 7½ for ferro-manganese, estimating manganese by difference. Thus:—

*Spiegeleisen.*

| | | |
|---|---|---|
| Iron .. .. .. .. .. | 84·25 | per cent. |
| Carbon, silicon, &c. .. .. | 6·00 | " |
| Manganese (by diff.) .. .. | 19·75 | " |
| | 100·00 | |

*Arsenic.*

Should arsenic be contained in the iron or steel, it will be precipitated along with the copper as sulphide, upon passing a current of sulphuretted hydrogen gas through a solution of the metal as previously described. For the separation of the two metals advantage is taken of the fact that sulphide of arsenic is soluble in hydrogen potassium sulphide (KHS), while copper sulphide is not.

The precipitate of mixed sulphides is digested with a moderate excess of hydrogen potassium sulphide, the insoluble copper sulphide collected on a filter, dissolved in nitro-hydrochloric, and the copper precipitated as oxide by means of caustic soda as previously described. To the filtrate remaining after treatment with KHS, add a small quantity of hydrochloric acid, collect the resulting precipitate of sulphide of arsenic on a filter, treat with carbon disulphide to remove free sulphur, rinse the precipitate into a beaker, and dissolve in nitro-hydrochloric acid. Filter, if necessary, and precipitate the arsenic as magnesium-ammonium arseniate, by adding to the *cold* filtrate a small quantity of magnesia mixture, and then a large excess of ammonia. Allow the solution to stand for twenty-four hours, collect the precipitate on a *weighed* filter, wash with ammonia water until a drop of the washings, after acidification, with nitric acid, gives only a slight opalescence with silver nitrate. Dry the filter and contents in a water oven, and convert the magnesium-ammonium-arseniate, contained in a weighed porcelain crucible, by ignition, at a *red heat*, into $Mg_2As_2O_7$, which contains 48·30 per cent of arsenic.

To prepare the magnesia mixture, dissolve 83 grms. of magnesia sulphate in water, add 5 c.c. of hydrochloric acid and 83 grms. of barium chloride dissolved in water. Filter a small portion of the solution, add a little sulphuric acid, and if a precipitate is formed add a further quantity of magnesia sulphate to the original solution. Filter, concentrate the filtrate, cool, add 165 grms. of ammonium chloride, together with 260 c.c. of ammonia, dilute to a litre. Allow to stand for a few days, and decant from any precipitate formed.

It is advisable to test all steels for this element, and it must be borne in mind that arsenic acid is precipitated together with phosphoric; the former must, therefore, be eliminated previous to the determination of phosphorus in steel, iron, &c.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, June 1st, 1893.*

Dr. ARMSTRONG, President, in the Chair.

MESSRS. T. L. BAKER, J. Addyman Gardner, James Mason, Robt. G. Grimwood, and Reginald B. Brown were formally admitted Fellows of the Society.

The certificate of Frank Browne, Government Civil Hospital, Hong Kong, was read for the first time.

Of the following papers those marked * were read:—

*25. "*Azo-compounds of the Ortho series.*" By R. MELDOLA, E. M. HAWKINS, and F. B. BURLS.

The constitution of the orthazo-compounds is still an unsolved problem owing to the contradictory results obtained by different investigators using different methods. The evidence in some cases points to the hydrazone formula and in others to the azo-formula, represented in the case of the azo-β-naphthols respectively by—

$$X{\cdot}NH{\cdot}N : C_{10}H_6 : O \text{ and } X{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH.$$

The compounds may really be isodynamic; but their acetyl and benzoyl, &c., derivatives, which were first investigated by one of the authors and G. T. Morgan (*C. S. Trans.*, 1889, 114), can hardly be thus regarded. The best evidence in favour of the hydrazone formula was furnished by Goldschmidt and Brubacher (*Ber.*, 1891, 2300), who obtained acetanilide and benzanilide by reducing the acetyl and benzoyl derivatives by means of zinc dust and acetic acid in alcoholic solution: these products are not obtained when stannous chloride is used as the reducing agent, a fact which was made known in 1889 in the paper referred to, and which has been confirmed in the present investigation.

In repeating Goldschmidt and Brubacher's work with the acetyl derivatives of ortho- and para-tolueneazo-β-naphthol, the authors have found that acetamido-β-naphthol is also one of the products of reduction, and in the case of a number of other acetyl derivatives this compound is found to be a normal product of reduction. Thus, in the case of an acetyl derivative of the form $X{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_2H_3O$ or $X{\cdot}N(C_2H_3O){\cdot}N : C_{10}H_6 : O$, four products are always obtained when zinc dust and acetic acid is the reducing agent, viz.:—$X{\cdot}NH{\cdot}C_2H_3O$, $C_{10}H_6(NH{\cdot}C_2H_3O){\cdot}OH\beta$, $X{\cdot}NH_2$, and $C_{10}H_6{\cdot}NH_2{\cdot}OH\beta$. The quantity of acetamido-β-naphthol is very small in the case of the acetyl derivative of benzeneazo-β-naphthol, a fact which accounts for this product having been overlooked by Goldschmidt and Brubacher. As the number of methyl groups in X is increased, the quantity of acetamido-β-naphthol increases, the acetyl derivative of pseudo-cumeneazo-β-naphthol giving about 9·2 per cent of this product when reduced by zinc dust and acetic acid in the manner described.

The following azo-compounds and their acetyl derivatives have been isolated and characterised in the course of the investigation:—

| | |
|---|---|
| *p*-Tolueneazo-β-naphthol (acetyl derivative) | Red prisms, m. p. 99°. |
| *p*-Chlorobenzeneazo-β-naphthol (acetyl derivative) | Flat needles or leaflets, red, m. p. 133°. |
| Pseudocumeneazo-β-naphthol | Bronzy prisms or bright scarlet needles, m. p. 163° to 164°. |

Other acetyl derivatives have been prepared, but used immediately for reduction for reasons explained in the paper. The acetyl derivative of benzeneazo-β-naphthol has been reduced under various conditions, and is always found to give a small quantity of acetamido-β-naphthol except when stannous chloride is used, when the chief product appears to be either a naphthylphenyl or a naphthylphenylamine derivative. The latter will be made the subject of a special investigation. Even when zinc dust and chlorhydric acid were used as reducing agents, acetamido-β-naphthol was obtained, but the quantity of acetanilide is in this case insignificant, the chief products being amido-β-naphthol and aniline.

The authors conclude that the formation of acetamido-β-naphthol on reduction is destructive of Goldschmidt and Brubacher's evidence in favour of the hydrazone formula for the ortho-azo compounds. The simultaneous formation of acetanilide, acettoluide, &c., and acetamido-β-naphthol cannot be explained by either azo- or hydr-azone formula alone; but if it be assumed that an intermediate product of the nature of an anhydro compound is formed, the production of these compounds is accounted for. It is shown in the paper that the same anhydro compound would be produced whether the acetyl group were attached to nitrogen or oxygen in the original compound, so that the question of the constitution of the ortho-azo compounds still remains an open one. Further experiments on the reduction of the acetyl and benzoyl derivatives of other ortho-azo compounds are in progress.

*26. "*The Production of a Fluorescein from Camphoric Anhydride.*" By J. NORMAN COLLIE, Ph.D., F.R.S.E.

Last year the author proposed a formula for camphoric acid of the succinic type (*Ber.*, xxv., 1116). Up to that date no fluorescein had been prepared from camphoric anhydride, and it had even been stated that this anhydride did not form such a compound (J. E. Marsh, *C. S. Trans.*, 1891, 651); it therefore seemed necessary to institute further experiments to obtain an explanation of this apparently anomalous behaviour of camphoric anhydride. The author finds that under suitable conditions camphoric anhydride is without difficulty converted into a fluorescein, the best results being obtained by heating one molecular proportion of the anhydride with two molecular proportions of resorcinol to about 180° C., with a relatively small amount of zinc chloride.

The resulting fluorescein, $(C_{22}H_{22}O_5)$, is a reddish-brown powder, which, when dry, has a greenish lustre. It dissolves in alkalis, affording a pink-coloured solution, and exhibits in dilute aqueous solutions a beautiful green fluorescence.

When sulphuric acid is employed in its preparation, the yield of fluorescein is small, the chief product being a brown compound which dyes cotton mordanted with alumina a pink colour.

The author finds that isopropylglutaric anhydride also furnishes a fluorescein, so that the production of a fluorescein from camphoric acid does not afford evidence which can be made use of in deciding whether the acid is a compound of the succinic or of the glutaric type.

*27. "*Researches on the Terpenes. III. The Action of Phosphorus Pentachloride on Camphene.*" By J. E. MARSH and J. A. GARDNER.

The authors describe the results of the further study of the action of phosphorus pentachloride on camphene. When these substances are allowed to interact without heat being applied, a mixture of camphene hydrochloride and a chlorophosphonic derivative of the formula $C_{10}H_{15}PCl_4$ is obtained. On treatment with water, the latter compound is converted into a mixture of acids which, together with the camphene hydrochloride, forms a syrupy mass, from which the acids are separated by fractionally extracting with a solution of sodium carbonate. After further purification by means of suitable solvents, two well-characterised isomeric camphenephosphonic acids of the formula $C_{10}H_{15}PO_3H_2$ were obtained.

*α-Camphenephosphonic acid*, crystallised from dilute alcohol, has a composition represented by the formula $2C_{10}H_{15}PO_3H_2+H_2O$. It is characterised by its insolubility in ether and ready solubility in chloroform; when heated at 100° it loses the elements of two molecules of water. The anhydrous acid melts at 184°. The acid is monobasic. The sodium salt crystallises from water or alcohol; the barium salt forms an almost insoluble crystalline precipitate.

*β-Camphenephosphonic acid*, crystallised from dilute alcohol, has the composition $C_{10}H_{15}PO_3H_2$. It does not lose weight when heated during several hours at 100°, but on prolonged heating it turns brown, melts, and loses weight. It is readily soluble in ether, but insoluble in chloroform; it melts at 170°. The acid is monobasic. The sodium and ammonium salts have been prepared.

The α- and β-acids further differ in rotatory power. When prepared from camphene having a rotatory power of $-60°$, the specific rotatory power of the α-acid was $[\alpha]_D = -119°$, and that of the β-acid $-71°$.

When the mixture of phosphorus pentachloride and camphene is heated, a crystalline compound of the formula $C_{10}H_{14}PCl_3$ is obtained, which has been previously described (*C. S. Trans.*, 1891, 652). When subjected to the action of a solution of sodium carbonate, this compound yields a sodium salt of the formula $C_{10}H_{14}ClPO_2NaH + 5H_2O$. The corresponding barium salt is soluble in water, and crystallises with three molecular proportions of water. The acid is an oil. On oxidation by potassium permanganate in alkaline solution it is converted into the corresponding *chlorocamphenephosphonic acid*, $C_{10}H_{14}PO_3H_2$. This may be crystallised from benzene; it melts at 178°, undergoing decomposition. When a mixture of camphene with a larger excess of phosphorus pentachloride is heated, and the product is hydrolysed, the same chlorocamphenephosphonic acid is obtained, together with an isomeric acid. The sodium salts of all these phosphonic acids are acted on by bromine, the phosphonic group appearing in solution as sodium phosphate, brominated derivatives of camphene being produced, which are under investigation. On oxidation by nitric acid, chlorocamphenephosphonic acid yields camphoic acid. On fusing chlorocamphenephosphonic acid with potash, a very small quantity of a crystalline volatile substance was obtained.

*28. "*The Composition of a Specimen of Jute Fibre produced in England.*" By ANDREW PEARS, Jun.

The author succeeded in securing a normal growth of the jute plant (*Corchorus capsularis*) in a "hothouse" of average temperature, 65° F. The stems, 5 feet in length and branched, were cut down after maturation of the seed, which has since been germinated for growth during the current year. The stem-fibre was separated after retting in tepid water, and was exhaustively investigated. It showed the characteristic behaviour of lignocelluloses, but with important variations in degree; the most marked difference observed was in ultimate composition, the carbon percentage being only 43 as against 46—47 in the normal fibre. From the results, given in full in the paper, it is shown that the factors of lignification induce variation in chemical composition, within wide limits, at the same time that the general constitutional type is preserved. Lignification may, in fact, be regarded as a gradual passage from "saturated" to "unsaturated" compounds, and as the result of the splitting off of water and carbon condensation, the specimen in question representing the earlier phases of such transition or evolution.

29. "*Note on the Combination of Dry Gases.*" By W. RAMSAY, F.R.S.

Mr. H. Brereton Baker has stated in his recent note that when dry ammonia is mixed with dry hydrogen chloride, these gases do not combine to form ammonium chloride; I would therefore call attention to a statement to the same effect by Dr. Sydney Young and myself in a paper on "Evaporation and Dissociation," published in the *Phil. Trans.*, 1886, Part I., p. 89. After describing the behaviour of ammonium chloride at 280° in a modified Hofmann's vapour-density tube, we state:—"When the tube cooled, a permanent gas remained, which exerted a pressure of 18·3 m.m. As a very long time was allowed so as to make certain of no further rise (of pressure) when the ammonium chloride was heated, the presence of this gas cannot be accounted for by a gradual decomposition of the ammonia, for we have shown (*J. Chem. Soc.*, 1884, 88) that ammonia begins to decompose only at 500°, even when hydrochloric acid is absent. It might, however, to some extent be due to the action of hydrochloric acid on mercury. On inclining the tube, this gas formed a bubble of considerable size at the top. Water was introduced, and almost complete absorption occurred. It appears certain, then, that gaseous hydrogen chloride and ammonia, when perfectly dry, combine very slowly."

These experiments were made in order to measure the vapour pressure of ammonium chloride; hence there was always a large excess of solid chloride present. It appears, therefore, that even in presence of the associated solid compound, the gaseous constituents may remain in presence of each other without combining.

I was not so successful as Mr. Baker has been in preventing the combination of nitric oxide and oxygen. Even after a bulb of nitric oxide containing several grms. of phosphoric anhydride—itself contained in a bulb of oxygen in which there was a considerable quantity of the anhydride—had been left during three months, on breaking the thin-walled inner bulb, a red colour was at once seen. I cannot but conclude that some substance other than water vapour may also have the power of effecting such combination; unless, indeed, it be contended that such a lengthened exposure to phosphoric anhydride does not completely dry the gases.

30. "*Ortho-, Para-, and Peri-disulphonic Derivatives of Naphthalene.*" By HENRY E. ARMSTRONG and W. P. WYNNE.

In a previous communication, dealing with the results of the examination of a large number of disulphonic acids (*Proc. C. S.*, 1890, 133), attention was drawn to the "'invincible objection' of two sulphonic radicles to *remain* in either contiguous or para- or peri-positions" relatively to one another when disulphonic acids are formed by the action of sulphuric acid either on naphthalene or on the chloro-, amido-, or hydroxy-naphthalenes. Further investigation has failed to supply a single exception to this rule, and it is noteworthy that of the known disulphonic acids only two—the No. II. α-naphthylaminedisulphonic acid of Dahl and Co.'s German Patent No. 41957 (*loc. cit.*, p. 125), and the minor product of the sulphonation of potassium 2 : 3′-chloronaphthalenesulphonate (*loc. cit.*, p. 132)—contain the two sulphonic radicles relatively in the positions 1 : 2′, the favoured positions being 1 : 4′, 2 : 4′, 2 : 2′, and 2 : 3′, the position 1 : 3 being taken up only in the case of sulphonation products of certain β-chloro- and β-amido-naphthalenesulphonic acids. Moreover, while the number of naphthalenedisulphonic acids obtainable, either by the sulphonation of naphthalene or by eliminating the $NH_2$ radicle from naphthylaminedisulphonic acids, amounts to six, it is very significant that only two naphthylaminetrisulphonic acids—the 1 : 3 : 2′- and the 1 : 3 : 3′-derivatives—can be obtained by sulphonating naphthalene, and that the only trisulphonic acids obtained by sulphonating the naphthols and naphthylamines contain their sulphonic radicles relatively in one or other of these positions.

While preparing the final account of our seven years' investigations, we endeavoured in various ways to prepare the missing acids containing the sulphonic radicles in the positions which are avoided in all products of direct sulphonation, so that their behaviour towards sulphonating agents might be studied in order that the explanation of this remarkable law of substitution might be given. While engaged in these experiments, we learnt with great satisfaction from Dr. C. Duisberg that a process had been devised in the laboratory of the Farberfabriken vormals F. Bayer and Co., of Elberfeld, which had enabled them to prepare all the acids we were in search of, and with that courtesy which is characteristic of German chemical manufacturers Dr. Duisberg at once communicated their method to us, so that we might proceed to study the various acids from the scientific side.

The process consists in displacing the amido-group in a naphthylamine derivative by SH and oxidising the resulting thio-derivative by means of alkaline permanganate; the thihydride is prepared by Leuckart's method (*J. Pr. Chem.*, [2], xli., 218) by submitting the diazo-compound prepared from the amine to treatment with potassium xanthate and hydrolysing the resulting xanthate. The thihydride thus formed being unstable in presence of oxygen, the corresponding disulphide is usually obtained. The process is described in the German Patend Anmeldung F. 6099, Cl. 22, of the Farbenfabriken vorm. Friedr. Bayer and Co., Elberfeld, in which an account is given of three new disulphonic, seven new tri-sulphonic, and two tetrasulphonic acids of naphthalene. With no more information before us than is afforded by the specification, we have been able without the slightest difficulty to prepare the various acids, and we have nothing to add to the admirable description given in the specification—a striking illustration of the character of the German chemical patent literature of the day.

In the present note only three new disulphonic and one new trisulphonic acid are referred to; the remaining acids will be described in a later communication. On treatment with phosphorous pentachloride, the 1 : 1'- and 1 : 2-acids yield products which apparently are the corresponding anhydrides. This behaviour is of interest as an extension of the observations made in V. Meyer's laboratory on the formation of anhydrides of disulphonic acids of thiophen. It is remarkable that the R-acid, in which there are two contiguous $\beta$-sulphonic groups, has not been found to yield an anhydride.

In the first instance, we availed ourselves of the method to prepare from the (Badische) 1 : 2'-$\beta$-naphthylamine-sulphonic acid the 1 : 2'-naphthalenedisulphonic acid previously discovered by us (*Proc. Chem. Soc.*, 1890, 125). The product is identical with that obtained from Dahl's No. II. $\alpha$-naphthylaminedisulphonic acid, and thus an independent proof is afforded of the somewhat remarkable constitution which we have assigned to this acid.

1 : 1'-*Naphthalenedisulphonic acid* was prepared from the Schöllkopf 1 : 1'-$\alpha$-naphthylaminesulphonic acid kindly placed at our disposal by the Actiengesellschaft für Anilinfabrikation, Berlin. The corresponding *potassium naphthalenesulphidesulphonate*, $(C_{10}H_6S{\cdot}SO_2K)_2 + H_2O$, crystallises in very small pale yellow scales, sparingly soluble in cold water. *Potassium* 1 : 1'-*naphthalenedisulphonate*, $C_{10}H_6(SO_3K)_2 + H_2O$, crystallises in well-defined, four-sided scales sparingly soluble in hot water; what appears to be the corresponding *anhydride* crystallises in small, rhomboidal, probably monosymmetric plates, melting at 227°, which are sparingly soluble in hot benzene, more soluble in hot xylene and acetic acid.

1 : 2-*Naphthalenedisulphonic acid* was obtained from the Landshoff and Meyer 1 : 2-$\alpha$-naphthylaminesulphonic acid. The corresponding *potassium naphthalenesulphidesulphonate*, $(C_{10}H_6S{\cdot}SO_3K)_2 + 4H_2O$, crystallises in pale yellow granules consisting of microscopic prisms sparingly soluble in cold water. *Potassium* 1 : 2-*naphthalenedisulphonate*, $C_{10}H_6(SO_3K)_2 + \frac{2}{3}H_2O$, crystallises from water in very soluble prismatic tables; what appears to be the corresponding *anhydride* crystallises from benzene, in which it is tolerably soluble, in elongated striated prisms melting at 198°.

1 : 4-*Naphthalenedisulphonic acid* was prepared from naphthionic acid. The corresponding *potassium naphthalenesulphidesulphonate*, $(C_{10}H_6S{\cdot}SO_3K)_2 + 2H_2O$, crystallises from water in easily soluble, pale yellow, microcrystalline granules. *Potassium* 1 : 4-*naphthalenedisulphonate*, $C_{10}H_6(SO_3K)_2 + 1\frac{1}{2}H_2O$, crystallises from water in small readily soluble needles; the corresponding *chloride*, $C_{10}H_6(SO_2Cl)_2$, crystallises from benzene, in which it is readily soluble, in four-sided, monosymmetric plates showing an optic axis just beyond the edge of the microscope field; this melts at 160°.

2 : 2' : 3'-*Naphthalenetrisulphonic acid* was obtained from 2 : 2' : 3-$\beta$-naphthylaminedisulphonic acid (amido-R-acid). The corresponding *potassium naphthalenesulphide-disulphonate*, $[C_{10}H_5S(SO_3K)_2]_2 + 5H_2O$, crystallises from water in finely striated prismatic forms having a beautiful velvet-like appearance. *Potassium* 2 : 2' : 3'-*naphthalenetrisulphonate*, $C_{10}H_5(SO_3K)_3 + 3H_2O$, crystallises from water in small, microcrystalline, spherical aggregates; the corresponding *chloride*, $C_{10}H_5(SO_2Cl)_3$, crystallises from benzene, in which it is tolerably soluble, in long, flat, probably monosymmetric plates showing longitudinal striations, melting at 200°.

The method of substituting the $SO_3H$ radicle for $NH_2$ has been extended to the chloro-$\beta$-naphthylamine-sulphonic acids, and in particular to the 1 : 2 : 2'- or "No. III." acid, with the object of comparing the product with the $\alpha$-chloronaphthalene-2 : 2'-disulphonic acid obtained from Alén's $\alpha$-nitronaphthalene-2 : 2'-disulphonic chloride, to which Cleve attributes a like constitution (*Ber.*, xxv,, 2490). We take this opportunity of stating that further investigation has shown that, contrary to our previously expressed view (*cf. Proc. Chem. Soc.*, 1890, 135), the No. 2 and No. 3 acids have an independent origin.

By the discovery of the disulphonic acids here described, we are now placed in possession of nine of the ten possible acids. We have previously characterised the ten possible dichloronaphthalenes and the two homonucleal trichloronaphthalenes (*Proc. Chem. Soc.*, 1890, 76, 77); we have now all but completed the study of the remaining twelve trichloronaphthalenes, having converted them into sulphonic acids, &c., in order that it may be possible to characterise them beyond question. So soon as the few remaining comparisons are completed, a detailed account of the investigation will be submitted.

Experiments are being carried out in the Central Institution laboratory by one of us with the object of determining, by means of the xanthate method, whether in the case of other hydrocarbons orthodisulphonic acids can be obtained which can exist in presence of sulphonating agents—the statements on record being far from satisfactory, and in some cases contradictory.

31. "*Supplementary Notes on Madder Colouring-Matters.* By E. SCHUNCK, Ph.D., F.R.S., and L. MARCHLEWSKI.

Many years ago (*Phil. Trans.*, 1853, 72) one of the authors described under the name of rubiadin a yellow colouring-matter obtained from madder. It is now shown that madder contains a glucoside of this substance, the preparation and properties of which are described. The glucoside crystallises in yellow needles melting at about 270°. On acetylation by Liebermann's method, it yields a pentacetyl derivative. On treatment with baryta-water it yields a dark red lake, one hydrogen atom being displaced by barium. On hydrolysis, it is converted into rubiadin and ordinary dextrose,—

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_4 + C_6H_{12}O_6.$$

Rubiadin crystallises in lustrous yellow needles melting at 290°. It very closely resembles purpuroxanthin, and is probably the corresponding derivative of methylanthracene.

32. "*The Constitution of Rubiadin Glucoside and of Rubiadin.*" By L. MARCHLEWSKI.

It is pointed out that of the five hydroxyl groups in rubiadin, one is phenolic, inasmuch as the glucoside yields dark red coloured mono-metallic derivatives; further, it is contended that probably glucose always exists in glucosides in the form of an anhydride of a hepta-hydric alcohol; a formula is assigned to the glucoside based on these arguments.

Assuming that rubiadin is derived from the same ($\beta$) methylanthracene as emodin, &c., it is pointed out that there are still three possible formulæ if rubiadin be regarded as a meta-dihydroxyanthraquinone—one homo- and two hetero-nucleal.

By heating a mixture of symmetrical metadihydroxybenzoic acid, parамethylbenzoic acid, and sulphuric acid at 110°, the author has obtained a substance of the same composition and closely resembling rubiadin, but melting at 267°.

## PHYSICAL SOCIETY.

*Ordinary Meeting, June 9th, 1893.*

Prof. J. Perry, F.R.S., Vice-President, in the Chair.

Prof. A. Jamieson, Prof. H. Stroud, and Mr. J. Wade were elected Members of the Society.

Mr. A. P. Trotter read a paper on "*A New Photometer.*" The author has modified his "Illumination Photometer," described *Proc. I.C.E.*, vol. cx., Paper No. 2619, so as to adapt it to the measurement of candle-power. The principle employed is to view a screen illuminated by one source through an aperture in a second screen illuminated by the other light, the aperture becoming invisible when the illuminations are equal. After using perforations of various patterns, a series of narrow slots cut in thin paper were found to give the best results. The plain screen is mounted behind the slotted one in a box sliding on the photometer bench, and they are arranged so that the light falls on them at equal angles. The screens are viewed, from a distance of 6 or 7 feet, through an opening in the front of the box, cords being provided for producing the traversing motion. Two "sights" set respectively at the middle of the length of the plain screen, and on the lower edge of the front opening, serve to show when the middle of the band of equal illumination is vertically above the pointer on the carriage. The photometer is found to be particularly valuable when it is desired to determine the maximum power of a variable source. When lights of different colour are being compared, say a gas-flame and an arc, one end of the screen shows blue strips on a yellow ground, and the other end yellow strips on a blue ground; at the centre the colours seem to blend. To facilitate the comparison of such lights, Mr. Crompton, who has been working at the subject simultaneously with the author, uses one screen tinted pale yellow and the other pale blue. Details of construction of the new photometer are given in the paper, and the accuracy attainable when comparing two equal lights of about eight candles is stated to be about 1 per cent.

Prof. S. P. Thompson, D.Sc., F.R.S., read "*Some Notes on Photometry.*"

The first note relates to "The Use of Two Overlapping Screens as an Isophotal," and describes the evolution of the Thompson-Starling photometer. In this instrument a prismatic block, with apex upwards, rests crosswise on the photometer bench, and the inclined sides are respectively illuminated by the two sources to be compared. In testing differently coloured lights, coloured stuffs were placed over the surfaces of the edge. In some cases notched and overlapping cards were used to form the overlapping surfaces. An inclination of about 70° between the two surfaces was found convenient.

The second note refers to the "Periodic Principle in Photometry," and in it the author discusses various methods which have been, or may be, used for producing small difference of decreasing amount between the two sides of a photometer screen. By employing a device of this kind much greater accuracy of adjustment is possible. In one form of vibration photometer worked out by the author, the paraffin blocks of a Jolly's photometer are mounted at one end of a spring, the other end being fixed to the carriage. The act of moving the carriage starts the blocks vibrating, thus producing the desired variations.

In a third note the question of using "The Electric Arc as a Standard of Light" is dealt with. Since 1878 the positive crater has been used as a standard of whiteness, and last year both the author and Mr. Swinburne suggested that a given area of crater might be used as a standard of light. This proposal has since been carried out by M. Blondel. Since the intrinsic brilliancy of the crater is high, it necessitates very small apertures, or else the use of standards of large candle-power. Advantages of using powerful standards are pointed out in the paper. With a circular hole 1 m.m. in diameter a standard of about fifty-five candles could be obtained; with such a source benches longer than usual would be preferable. At the end of the note the errors which may be introduced by using, as an arc standard, a hole in a plate of sensible thickness, when viewed obliquely, are investigated, as well as those due to inaccuracy of setting the plane of a hole made in foil perpendicular to the photometer bench.

Major-General Festing, in opening the discussion on both papers, said reflection from the sides of the hole in a thick plate would tend to lessen the error calculated by Prof. Thompson. The ordinary impurities in carbon were not likely to alter the brilliancy of the crater. Capt. Abney and himself had no reason to distrust its constancy. Both the vibrating photometer and Mr. Trotter's arrangement would be very useful.

Dr. Sumpner said his photometric experience had been obtained with the Bunsen, Jolly, and Lummer-Brodhun types. With the two former the inaccuracy arising from uncertainty of adjustment was about ½ per cent.; changes of about 0·4 per cent (average) resulted from reversing the screens. The Lummer-Brodhun instrument (which he described) was better than either of the other two, the average error being about ¼ per cent.

Mr. Frank Wright thought scientific men gave too little attention to the question of light standards. Photometers could be relied on much more than any standard at present in use. The Methven screen was the most practical standard yet devised, but in his opinion no gaseous flame could be a real standard on account of the influence of the surrounding atmosphere.

Prof. Ayrton saw difficulties in using long benches as suggested by Dr. Thompson, on account of the serious atmospheric absorption which occurs with light from arcs. Decreasing the intensity by dispersion or otherwise was preferable. In some tests on glow lamps now being carried on at the Central Institution, a Bernstein lamp used as a standard was mounted on a spring and vibrated.

Mr. Medley showed the vibrating standard referred to by Prof. Ayrton, and gave a series of numbers showing that with this device in conjunction with the Lummer-Brodhun photometer accuracies of about ¼ per cent were obtainable.

Mr. Swinburne thought Mr. Trotter's arrangement was better than the "wobbling" photometer. As to the best length of bench he was inclined to think the shorter the better, provided its dimensions were large compared with those of the standard light. He concurred with Mr. Wright in his remarks about the desirability of obtaining a better standard. Speaking of the arc as a standard he said that only impurities less volatile than carbon would influence the brightness. An important factor was the emissivity of the carbon, which might not be constant.

Mr. Blakesley thought the accuracy obtainable with Mr. Trotter's photometer had been underrated, and pointed out that by using quadrant-shaped screens intersecting orthogonally on the axis of the photometer instead of straight ones, the width of the neutral band could be greatly diminished.

Mr. Trotter, referring to Dr. Thompson's paper, said he had found considerable difficulty in making pin-holes suitable for arc standards. It was not an easy matter to accurately measure the hole when made. In photometric measurements he had found it very important to reverse his screens. Curved screens, as suggested by Mr. Blakesley, had been tried, but with little advantage. They also destroyed the approximate direct-reading property of the photometer. The subject of changing the length of a bench and its effect on the gradient of illumination was discussed. With short benches one had to guard against the departure from the inverse-square law, due to appreciable size of the standard. Recent experiments had shown that the light given out by 1 square m.m. of crater surface differed considerably from 70 candles.

A paper on "*The Magnetic Field close to Surface of a Wire Conveying an Electric Current*," by Prof. G. M. Minchin, M.A., was taken as read. In this paper the author applies the solution he gave in March last for the conical angle subtended by a circle at any point in space to determine the negative potential at a point near the surface of a ring of wire of circular cross section. The shapes of the lines of force near the surface, for several laws of current distribution across the section, have also been worked out.

## CORRESPONDENCE.

### ON THE ANALYSIS OF PIGMENTS WHEN GROUND IN OIL.

*To the Editor of the Chemical News.*

Sir,—Referring to Mr. J. B. Hannay's paper under the above title in the Chemical News, lxvii., 268, the method usually adopted for the extraction of oil from white-lead is to treat from 30 to 50 grms. in a Soxhlet apparatus with methylated ether (absolute), removing the white-lead after, say, four hours, drying and grinding, and re-extracting with ether until on testing no further oil is obtained.

If the greater part of the ether be removed by evaporation, and the residue, after filtration through several Swedish filters, tested by passing sulphuretted hydrogen, a distinct trace of lead sulphide is always obtained. Even adopting the process of extraction suggested by Mr. Hannay (which would be impracticable in commercial work), on evaporating down the large volume of ether used to a small bulk, a trace of lead is found. Thus in an experiment with 50 grms. of Stack white-lead and 5 litres of ether, a distinct trace of lead was obtained, and also a trace of oil on dissolving the 50 grms. in nitric acid.

I fear that it will be a very long time before Mr. Hannay succeeds in educating the "ignorant tradesman" to use his so-called white-lead (sulphate of lead) in preference to that made by the Stack process.—I am, &c.,

R. H. Harland.

37, Lombard Street, E.C.,
June 15, 1893.

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**The Odoriferous Power in the Fatty Series.**—Jacques Passy.—In an odoriferous substance the author distinguishes three properties,—the power, the intensity, and the quality. The power is the inverse of the minimum perceptible. The minimum perceptible of camphor being 5 and that of vanilla 0·005 in millionths of a grm., the odoriferous power of vanilla is 100 times that of camphor. Of two odours, the more intense is that which masks the other. The following Table gives the substances in the order of their power, which is almost the inverse order of their intensity:—Camphor, 5; ether, 1; citral, 0·5 to 0·1; piperonal, 0·1 to 0·05; coumarine, 0·05 to 0·01; vanilline, 0·005 to 0·0005. The quality is that which distinguishes one odour from another.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 11.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 22, May 29, 1893.

**The Volatilisation of Silica and Zirconia, and the Reduction of these Compounds by Carbon.**—Henri Moissan.—This paper will be inserted in full.

**Preparation in the Electric Furnace of the Refractory Metals, Tungsten, Molybdenum, and Vanadium.**—Henri Moissan.—This paper also will be inserted in full.

**The Preparation of Zirconium and Thorium.**—L. Troost.—This paper will be inserted in full.

**Observations on the Volatilisation of Silica, with Reference to the Communication of M. Moissan.**—P. Schützenberger.—I have heard with the warmest interest the important communication of M. Moissan. The fact which he has distinctly established—of the volatility of silica at a very high temperature—supplies the explanation of phenomena which I observed a long time ago in the course of a research executed in concert with M. Colson, phenomena which in my opinion ought to incite to further researches. We observed:—1. That pure silica placed in small crucible of retort coke enclosed in a larger crucible lined with lamp-black and heated for some hours in a good blast furnace, loses a notable quantity of its weight. 2. That platinum gains weight, becomes fusible, and takes up silicon, even if placed in a covered crucible of coke, plunged in a thick "brask" of lamp-black, and heated to whiteness for two hours. This effect is not produced if the lamp-black is replaced by a mixture of black and of rutile in powder, but if we introduce silica into the crucible of coke containing the platinum and separating the two substances by a plate of coke, the platinum becomes loaded with silicon and melts even in a titaniferous "brask." Silicon substituted for silica has no action, and does not seem to be volatile. All these facts are easily intelligible if we admit, as M. Moissan has proved, the volatility of silica.

**Action of Acetic Anhydride upon Linalol; Transformation into Geraniol.**—G. Bouchardat.—According to the experiments of the author, linalol or licaréol modified by etherification appears identical with geraniol. Consequently the aldehyd derived from linalol is identical with geraniol, of a citron odour, $d_0$=c·898.

**General Method for the Analysis of Butters.**—Raoul Brullé.—This paper will be inserted in full.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 9.

**Monobromgallic Acid and its Derivatives.**—Alex. Biétrix.—This acid contains three molecules of crystalline water. The author has obtained and examined the ammonium lead, monobromogallates, and the triacetylmonobromgallic acid.

**New Process for Obtaining Oxyhæmoglobine by means of Oxyhæmatine and an Albumenoid Substance.**—H. Bertin-Sans and J. Moitessier.—The authors' process renders it possible to obtain, extemporaneously by means of solutions of oxyhæmatine and of albumenoid matter, very concentrated solutions of a compound which presents very distinctly the appearance and the spectral reactions of hæmoglobine, and containing no impurities except a slight excess of the albumenoid matter.

**The Féry Refractometer.**—This paper requires the accompanying illustrations.

**Determination of Manganese in its Ores and its Alloys.**—Ferdinand Jean.—This paper will be inserted in full.

**Analysis of Impure Galenas and New Method of Determining Copper and Zinc.**—Ferdinand Jean.—This paper also will be inserted in full.

**Volumetric Determination of Copper, Iron, Antimony, and Zinc in Powder.**—Ferdinand Jean.—The substance of this paper has been already noticed.

**Use of Superphosphates.**—Jules Joffre. — Already inserted.

**Manufacture of Extracts of Dye-woods.**—A. and P. Buisine.—This article consists of extracts from a memoir on the subject which appeared in 1891 in the *Bulletin de la Société Industrielle de Mulhouse.*

**Concentration of Sulphuric Acid.** — A. and P. Buisine.—This bulky paper requires the ten accompanying cuts.

## MEETINGS FOR THE WEEK.

Tuesday, 27th.—Photographic, 8.
Wednesday, 28th.—Society of Arts, 4. (Anniversary).
—— British Astronomical Association, 3,

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1753.

## VEGETATION IN HYDROGEN.

By Dr. T. L. PHIPSON, F.C.S., &c.,
Graduate of the Faculties of Science and Medicine of the University of Brussels.

In a recent paper, in which I made known the views of the late Prof. Koene on the constitution of the atmosphere at remote periods of the earth's history,* I promised to continue my experiments with carbonic acid.

From Koene's view that no free oxygen could have existed in the atmosphere when life first appeared on the globe, because we find oxidisable substances in the primitive rocks, and that the original atmosphere of the globe at that period was formed exclusively of carbonic acid and nitrogen, it follows, as I hinted before, that oxygen—the essential element of modern life—must have been derived from the vital functions of inferior plants, from the *protoctista*, or first created living beings, having the power of separating it from its compounds, carbonic acid and water.

It therefore became interesting to ascertain to what extent our modern plants can vegetate in carbonic acid, and to extend this inquiry to hydrogen and nitrogen.

I had noticed, many years ago, that certain plants (willow, lilac, &c.) did not thrive in an excess of carbonic acid, and concluded that the diminished quantity of this gas now existing in our air was the condition which suited them best. In experiments carried out this year, I have placed various other plants (*Poa*, *Myosotis*, *Antirrhinum*, and *Convolvulus*) in an atmosphere composed of pure carbonic acid, and in an atmosphere composed of air with about 100 times more of this gas than exists in our atmosphere. All other conditions of vegetation were normal: there was ample water, mineral elements, and an appropriate temperature (59° to 70° F.) during the course of the observations.

I found that my plants could exist for many days, or even weeks, in an atmosphere of pure carbonic acid, but they did not thrive; cell formation became slower and slower. In an atmosphere containing so much carbonic acid that an animal exposed to it would perish *in a few minutes*, plants lived for many *weeks* and appeared healthy. In an atmosphere containing 100 times as much carbonic acid as in the natural state of the air, plants flourished remarkably well for the whole time the experiment lasted (a month to six weeks).

It is therefore highly probable, as Koene held, that in former geological periods (the coal period, for instance) there existed plants which could live in an atmosphere excessively rich in carbonic acid, and that the quantity of that gas in the air has really decreased from that time to this, the loss being represented by the vast deposits of peat, lignite, coal, and anthracite found in the strata of the earth.

My next experiments were made with pure hydrogen gas, to see what would happen when plants are placed in an atmosphere consisting of nothing but hydrogen (a gas which many look upon as the vapour of a metal); all other conditions being normal, namely, water charged with carbonic acid and containing the necessary mineral elements.

The plants I placed in an atmosphere of pure hydrogen were *Convolvulus arvensis* (a plant which is very hardy and convenient for observations of this kind), and *Antirrhinum majus*.

For the first few days nothing peculiar was noticed. From May 27 to the end of the month, a slight bleaching of the leaves only was apparent, but by June 3 a singular phenomenon occurred: *the volume of gas began to diminish*, and in the course of a month the atmosphere of hydrogen in which vegetated the *Convolvulus* was absorbed to the extent of about 80 per cent. The residue, 20 per cent, was not hydrogen; so it may safely be said that *the whole of the hydrogen had disappeared*, the plant remaining perfectly healthy.

I explain this by assuming that the nascent oxygen emitted by the leaves burns up the hydrogen.

The same thing occurred with the *Antirrhinum*, but the action was slower. In both cases the leaves were slightly bleached, more decidedly so in the latter case; and as the water charged with carbonic acid rose in the vessel and covered them, they became greener again.

In all these experiments the plants were exposed to the constant light of a northern sky. The rapidity of cell formation in hydrogen gas observed in the case of *Convolvulus arvensis* is highly remarkable.

Putney, June 23, 1893.

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* Phipson, "Chemical Constitution of the Atmosphere from remote Geological Periods to the Present Time," Chemical News, vol. lxvii., p. 135.

## THE ACTION OF SILICON ON THE METALS GOLD, SILVER, PLATINUM, AND MERCURY.

By H. N. WARREN, Research Analyst.

With regard to the action of silicon on the more common metals,—iron and copper,—so well known are the properties in general of these elements when combined, that little, if any, comment is required; but on passing to the more refractory metals a much wider field for study is presented. As recorded by the various handbooks of chemistry, silicon, when in the nascent state, converts platinum into a brittle silicide.

This is by no means, however, the only method available for preparing this compound; for on heating graphitoidal silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus, being fusible at a red heat, and breaking with a crystalline fracture, at the same time being difficultly soluble in acids. The same compound may be more readily formed by heating in a closed crucible a mixture of amorphous silicon and platinum-black under a layer of potassium silico-fluoride; the analysis of several samples thus obtained proved the existence of 10 per cent silicon. On the other hand, neither silver or gold present any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride, metallic sodium, and either gold or silver in the amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance the alloy, containing as little as 5 per cent silicon, is almost as brittle as antimony, and resembles gold alloyed with a large proportion of silver. At the same time, although silicon possesses no considerable affinity towards either gold or silver, except when in a nascent state, still that affinity appears to be considerably enhanced by combining with either metal when in the fused condition a small quantity of an already prepared silicide. Thus, if on to the surface of a quantity of either silver or gold in the fused condition is ejected a few grains of an already prepared silicide of either gold or silver, complete mixture of the same at once ensues. This alloy, although containing but a minute percentage of silicon, may be raised to a much higher rate by the introduction of elementary silicon, which before this period showed even at elevated temperatures no special affinity, except when in a nascent form. Silver, when thus impregnated with from 10 per cent of silicon, becomes of a slightly red tint, resembling in appearance metallic manganese.

The regulus, after being pulverised, is completely decomposed by the aid of concentrated hydriodic acid. As regards the action of silicon on metallic mercury, nothing very definite can at present be stated; but on subjecting a small vessel containing mercury in contact with an alcoholic solution of silicon fluoride to the action of a powerful battery, and afterwards subjecting the mercury to distillation, a small quantity of amorphous silicon was obtained, but whether silicon, when in a nascent state, combines with, or is soluble in, mercury still presents considerable doubt.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

# A REVIEW OF RECENT INVESTIGATIONS UPON CARBOHYDRATES.*

By W. E. STONE.

These notes are intended to include the more important contributions to the subject during the past year without reference to technical matters.

In most cases the original papers are referred to for details, and only their leading features are given here on account of lack of space.

### *New Sugars.*

Some new members of the group of natural sugars have been identified, of which the *Stachyose* (E. Schulze and A. von Planta, *Land. Versuch Stat.*, xl., 277; and xli., 123) is best characterised. It has been isolated from the tubers of *Stachys tubcrifera*, where it occurs to the extent of 14 to 19 per cent of the fresh material. It is very sweet, without action on Fehling's solution, and with a specific rotation $(\alpha)_D = +147{\cdot}9^{\circ}$. It belongs to the trisaccharides or "trioses," with a formula corresponding to $C_{18}H_{32}O_{16},3H_2O$. On inversion, it breaks up into dextrose, levulose, and galactose, but in different proportions than raffinose. Probably the molecule is larger than indicated by the above formula, and its inversion products are, galactose three parts, dextrose two parts, and levulose one part.

*Fucose* (Günther and Tollens, *Annalen d. Chemie*, cclxxi., 86) is another new sugar obtained by heating a species of alga (*Fucus*) with dilute sulphuric acid. It is strongly lævorotatory $(\alpha)_D = -75{\cdot}96^{\circ}$, and shows marked multirotation; reduces Fehling's solution; yields an "osazon" melting at 158—160°, and has the formula $C_6H_{12}O_5$. It is isomeric with rhamnose. It yields methyl-furfurol, and is regarded as a methyl-pentose. Calorimetric observations indicate that it is methyl-arabinose (Stohman and Langbein, *J. Prakt. Chem.*, [2], xlv., 305).

*Agavose* (Michaud and Tristan, *Am. Chem. Journ.*, xiv., 548) is an optically inactive sugar obtained from the juices of *Agave Americana*. After inversion it becomes lævorotatory $(\alpha)_y = -14{\cdot}39^{\circ}$. It is very sweet, and reduces Fehling's solution about five-eighths as strongly as dextrose. It yields no mucic acid on oxidation. Further investigation of the sugar will be awaited with interest, as it is probably the source, by fermentation, of the alcoholic constituents of the Mexican "pulque."

*Lupeose* (E. Schulze, *Ber. d. Chem. Ges.*, xxv., 2213) is the name given to one of the insoluble amorphous constituents of the coat of the lupine seed. It is not a sugar, but yields on inversion galactose, levulose, and probably dextrose. It has previously appeared in literature as β-galactan (E. Steiger).

### *Progress on Synthetical Lines.*

The series of syntheses accomplished by Fischer and reviewed in *Agricultural Science* (vol. vi., 166) has been less actively extended of late. Admitting any ketone or aldehyd alcohol to be a sugar, as Fischer proposes, then the glycol aldehyd, $CH_2OH,CHO$, which he has prepared sparingly, is the simplest form of a sugar. There is an objection to this on the ground of optical inactivity, although it otherwise satisfies the conditions, reducing Fehling's solution, combining with phenylhydrazin and polymerising to tetrose, $C_4H_8O_4$ (E. Fischer and Landsteiner, *Ber. d. Chem. Ges.*, xxv., 2549).

It has also been shown that mucic acid could be reduced to an inactive monobasic acid which was then separable into two optically opposed isomers; one of which was d. galactonic acid; the other, a new body, l. galactonic acid. The inactive acid was reduced to inactive galactose, which after undergoing partial fermentation left behind l. galactose, thus completing the series of optical isomers of galactose (E. Fischer and J. Hertz, *Ber. d. Chem. Ges.*, xxv., 1247). By reduction of phenyl-tri-oxy-butyric acid by methods practised in his previous investigations, Fischer has also succeeded in producing a phenyl-tetrose, combining the properties of a benzine derivative and a sugar (E. Fischer and Stewart, *Ber. d. Chem. Ges.*, xxv., 2555).

### *Pentoses.*

Of the sugars which have already obtained a place in literature, the pentoses have received a good share of attention of late. Considerable effort has been expended in the development of methods for determining the amount of pentosans in vegetable materials. As a result of studies by Tollens and his pupils, the method of distilling with HCl, and precipitation and weighing of the furfurol by phenylhydrazin is regarded as satisfactory. By this method they obtained from xylose direct 52 per cent and from arabinose 43 per cent of furfurol, and have shown that many crude materials contain large amounts of pentosans; for instance, wheat straw yielded 21·90 per cent; corn cobs, 30·94 per cent; and brewers' grains, 27·00 per cent of furfurol (Tollens, Günther, and de Chalmot, *Land. Versuch Stat.*, xl., 11—17; Tollens and Flint, *Ber. d. Chem. Ges.*, xxv., 2912).

Bearing on this furfurol reaction as a means of determining the pentoses and pentosans, it has been found that glucuronic acid and its derivatives also yield furfurol in appreciable quantities, although under no ordinary circumstances would this lead to confusion on account of the rarity of glucuronic acid (Tollens, Günther, and de Chalmot, *Ber. d. Chem. Ges.*, xxv., 2569).

Experiments undertaken to ascertain if the pentoses (xylose) might be substituted for other sugars in the food of diabetic patients, have shown that the former, even though very soluble, are little if at all assimilated, and may be detected in the urine in a short time after consumption. Slight traces of the pentoses may be recognised in the urine by means of the phloroglucin reaction (*Central Bl. f. Med. Wissens.*, W. Ebstein, 1892, 577; E. Salkowski, 1892, 593. *Archiv. f. Path. Anat.*, W. Ebstein, cxxix., 401).

Investigations directed at the digestibility of the pentosans contained in feeding stuffs, shows that they are by no means completely digestible, probably much less so than the other amorphous carbohydrates of the same solubility (W. E. Stone, *Am. Chem. Journ.*, xiv., 9; *Agricultural Science*, vii., 6).

Neither of the pentoses has yet been found in nature as a free occurring sugar, although late researches seem to indicate the presence of slight traces in the green organs of plants as migratory material between assimilating organs and reserve tissues (G. de Chalmot, *Am. Chem. Journ.*, xv., 21).

On the other hand, the occurrence of the pentosans in new materials has been frequently noted. Xylose has been prepared from *Luffa* (fibro-vascular tissue of the fruit of a species of *Cucurbitaceæ*) by direct hydrolysis (Tollens and Schulze, *Land. Versuch Stat.*, xl., 381; also Tollens and Allen, *Ann. d. Chem.*, 260, 297). The pentosans of brewers' grains, already shown to yield both xylose

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* From *Agricultural Science.*

and arabinose, have been found to consist principally of the mother substance of xylose (Tollens and Schulze, *Land. Versuch Stat.*, xl., 367). The mucilage produced from quince seeds also yields xylose on inversion (*Ibid.*, 382; also Tollens and Gans, *Ann. d. Chem.*, ccxlix., 245). Xylose has been found in the liquors resulting in the manufacture of wood pulp by the "sulphite" method (Tollens and Lindsey, *Ann. d. Chem.*, cclxvii., 341). It has also been prepared from the alkaline liquors resulting from the pulping of straw in paper making (Stone and Test, *Am. Chem. Journ.*, xv., 195). In the coffee berry a pentosan has also been found, but the derivative pentose was not isolated (E. E. Elwell, *Am. Chem. Journ.*, xiv., 473). In this case the pentosan seemed to be present as a complex of pentosan and galactan, for the apparently homogeneous substance yielded both furfurol and mucic acid. A similar complex has already been proven in the gum exuding from the peach tree (Stone, *Am. Chem. Journ.*, xii., No. 6). Such a galacto-araban has also been found in the seeds of certain Leguminosæ, and in the bran of wheat and rye. These pentosans seem to be intimately connected with the ultimate cellular frame-work of the plant, and persist in connection with the fibre after the action of strong acids and alkalis (E. Schulze, *Chem. Centralblatt*, 1892, i., 701).

The specific rotation of xylose has been carefully worked out and found to be somewhat dependent upon temperature and concentration; for 10 per cent solution and 20°, $(\alpha)_D = 18\cdot794$ (Tollens and Schulze, *Land. Versuch Stat.*, xl., 384).

The resistance of arabinose and xylose to the continued action of dilute sulphuric acid has been found to be considerable. After twenty hours boiling with 4 per cent acid only slight decomposition had occurred, and after thirty-two hours 84 per cent of arabinose and 73 per cent of xylose were unchanged (Tollens and Schulze, *Land. Versuch Stat.*, xl., 379).

Arabinose, which is not susceptible to alcoholic fermentation by yeast, succumbs to an organism named *Bacillus ethaceticus*, yielding ethyl alcohol and acetic acid, $CO_2$ and H, with traces of succinic acid. It appeared that more acetic acid in proportion to the alcohol was found than by a similar fermentation of dextrose or glycerin (Frankland and McGregor, *Journ. Chem. Soc.*, lxi., 737).

### *Hexoses.*

*Dextrose.*—Some new sources or occurrences of dextrose have been announced. From the mucilage obtained from the coatings of quince seeds it was obtained by hydrolysis (R. W. Bauer, *Land. Versuch Stat.*, xxxix., 469); from the cellulose left in the manufacture of wood pulp by the "sulphite" process, in the same way (Tollens and Lindsey, *Annalen d. Chem.*, cclxvii., 370); by decomposing digitonin by heating with hydrochloric acid (H. Kiliani, *Archiv. der Pharm.*, ccxxx., 261).

Of unusual interest is the additional proof of dextrose in the blood, which has long been known to reduce Fehling's solution, ferment, and rotate polarised light. From blood has now been prepared a phenylhydrazin compound corresponding wholly with phenyl-glucosazon (Max. Pickardt, *Zeit. f. Physiol. Chem.*, xvii., 217). An octacetyl derivative of dextrose, as announced by Franchimont and later by Ewig and Koenig, has been found to be after all only a pentacetyl compound existing in isomeric form, one of which is optically inactive, and the other dextro-rotatory (A. Franchimont, *Recueil d. Traveaux Chim. de Pays bas*). It has been noted that aceton is appreciably soluble in solutions of dextrose, as well as other sugar, and this solubility at different concentrations and temperatures has been determined (W. Krug. *Am. Journ. Anal. and Appl. Chem.*, 1892, 189).

*Levulose* has been identified in thirty-six different species of fungi (E. Bourquelot, *Wochenschrift f. Brauerei*, viii., 908). Its specific rotation, as determined by calculation from the constants of invert sugar and of dextrose, is announced as $(\alpha)_j = -106^\circ$, or $(\alpha)_D = -93\cdot8$ (O'Sullivan, Chem. News, lxv., 165); and these numbers agree with those of Ost ($-93\cdot01$) and Tollens ($-92\cdot5$) fairly well. A former statement that levulose yielded mucic acid upon oxidation has been reviewed by its author and found to be incorrect (Von Lippmann, *Berichte der Chem. Gesell.*, xxv., 3216). A method for the quantitative determination of levulose in the presence of dextrose and sucrose will be mentioned later.

*Galactose* has been obtained from the liquor resulting from the sulphite wood-pulp process (Tollens and Lindsey, *Annalen d. Chem.*, cclxvii., 341), and from the complex *lupeose* in common with levulose and dextrose (E. Schulze, *Berichte d. Chem. Gesell.*, 2213); also by the decomposition of digitonin by means of alcoholic hydrochloric acid (H. Kiliani, *Archiv. f. Pharm.*, ccxxx., 261). The synthetic inactive galactose has already been noted.

*Mannit and Mannose.*—Mannit has been found in many different species of fungi amounting in some to from 2 to 15 per cent (E. Bourquelot, *Wochenschrift f. Brauerei*, viii., 908). Mannose was found with other sugars in the sulphite liquors from wood pulp (*loc. cit.*), and has been obtained by inversion of one of the more easily soluble forms of cellulose ("hemi-cellulose"). In the more resistant "cellulose" a substance is thought to exist (mannoso-cellulose) which on inversion yields dextrose and mannose (E. Schulze, *Chem. Centralblatt*, 1892, i., 701) From experiments, the physiological action of mannose is said to resemble that of galactose; it is excreted strongly in the urine, and is accompanied by the occurrence of small amounts of glycogen (Cremer, *Centralblatt f. Physiologie*, vi., 396).

Bearing upon the constitution of mannit is the fact that it forms a hexaiodide which may be transformed into a secondary inactive alcohol. This on being acted upon by fungi left behind a dextro-rotatory product which was regarded as ethyl-propyl-carbinol (Combes and LeBel, *Bull. de la Soc. Chim. de Paris*, [3], vii., 551).

*Dulcit* and *Mannit* are subject to a kind of fermentation by *Bacillus ethaceticus* (see arabinose) yielding ethyl alcohol, acetic acid, succinic acid, $CO_2$, and H (Frankland and Frew, *Journ. Chem. Soc.*, lxi., 264). Conflicting statements as to the activity or inactivity of dulcit have been current; the acetyl compounds have been said to be active. Upon a re-investigation they prove to be inactive, and thereby almost the last obstacle to the theory of optical activity in the sugar group is removed (A. W. Crosby, *Berichte d. Chem. Gesell.*, xxv., 2564).

*Isodulcit* or *Rhamnose*, $C_6H_{12}O_5$, although no new substance, has been of uncertain classification. It has been found to yield methylfurfurol when heated with HCl, and not levulinic acid, which shows that its nucleus is a pentose and not a hexose. Its specific rotation for anhydrous material is $(\alpha)_D = 9\cdot43^\circ$ at 20° C. (Schnelle and Tollens, *Annalen d. Chem.*, cclxxi., 62). By determination of its temperature of combustion when compared with those of xylose and arabinose is indicated a relation to the former (Stohman and Langbein, *Journ. Prakt. Chem.*, [2], xlv., 305). (See Fucose). It is, therefore, fairly well established as a methyl-xylose.

### *Disaccharides.*

The presence of *sucrose* has been determined in the coffee berry, where from 6·24 to 6·34 per cent was found in the alcoholic extract (E. E. Elwell, *Am. Chem Jour.*, xiv., 473). The solubility of aceton in solution of cane-sugar of strengths from 10 to 50 per cent, and at temperatures from 15° to 35°, has been determined (W. H. Krug, *Jour. Anal. and App. Chem.*, 1892, 89). Maltose has also been studied in the same respect.

It was noted some years ago that *lactose* existed in two optical modifications. In the light of recent developments the author has thought best to review his work, and finds it to have been correct; moreover, these modifications have the same molecular weight, refractive exponents, and degrees of dispersion. The statements of Herzfeld about the formation of an octacetyl derivative are substantiated by the same author (M. Schmöger, *Berichte d. Chem. Gesell.*, xxv., 1452).

*Isomaltose* may now be prepared with comparatively little trouble by acting on starch-paste with diastase at 67—69°, and separation from by-products by treatment with strong alcohol. In this way 20 per cent of the starch may be obtained as isomaltose (Lintner and Düll, *Zeit. f. das ges Brauereiweisen*, xv., 145).

### *Trisaccharides.*

*Raffinose* is said never to occur in the sugar-beet itself, and hence does not interfere with the determination of sucrose in that material. It is a product of manufacturing processes, but is no molasses former, and does not prevent crystallisation of the sucrose. The only reliable method for determining raffinose in sugar products is that of Clerget as modified by Herzfeld (A. Aulard, *Zeit. fur Rüb. Zuck. Ind.*, 1892, 752).

### *Miscellaneous.*

The action of diastase upon starch has been studied by different investigators, and the products seem to be very complex; beside the isomaltose already mentioned there seems always to be found malto-dextrin, achroodextrin, erythro-dextrin, and dextrin (Anton Schiffer, *Neue Zeit. f. Rüb. Zuck. Ind.*, xxviii., 167). Some new methods for the analytical determination of starch have also been presented, for which see below.

*Perseit* has held a rather indefinite place with regard to the better studied carbohydrates. Fischer found that the heptatomic alcohol derived from the reduction of manno-heptose was identical with the natural perseit, thus establishing its synthesis. By reduction with hydroiodic acid it becomes $C_7H_{14}$, called heptin, which has been found to be identical with toluol-hexahydrin, thus presenting an unexpected transition from the fatty to the benzene hydrocarbons (L. Maquenne, *Compt. Rend.*, cxiv., 1066). Perseit is optically active (lævo-rotatory), Upon addition of a soluble molybdate to its watery solution it becomes dextro-rotatory (D. Gernez, *Compt. Rend.*, cxiv., 480).

### *Multi-rotation.*

The well-known property of many sugars to exhibit a different degree of rotation immediately after solution in cold water, than after standing some hours, has been carefully studied for several sugars not previously investigated and several of their derivatives. An interesting observation in this connection was, that if a very small amount of ammonia be added to such a solution the multi-rotation disappears. 0·1 grm. of ammonia suffices to produce this result, and a larger amount even decreases the normal rotation (Tollens and Schulze, *Land. Versuch Stat.*, xl., 387).

### *Analytical.*

With regard to the saccharimetric coefficient for glucose the suggestion is made of a new constant, by which each degree of the saccharimeter should represent not 3·28 grms. of anhydrous dextrose in the litre as at present, since this is based on the specific rotation of dextrose calculated to anhydrous material. In place of this, 2·06 grms. of water-free dextrose in the litre is said to give a rotation of one degree, and should be the true saccharimetric constant (L. Grimbert, *Jour. Prakt. Chem.* [5], 26, 253).

For the determination of invert sugar by Herzfeld's method, a new constant for small quantites of sugar has been worked out. It was not always possible to use 10 grms. of material as demanded by Herzfeld's method, nor was it correct to use 5 grms. of material and multiply the results by two. A new table for 5 grms. has been completed (see original paper, or *Chem. Centralbl.*, 1892, 2, 997). By the method of least squares this formula has been deduced, $x$ indicating copper obtained. Invert sugar $= 0{\cdot}3164 + 0{\cdot}010054x + 0{\cdot}000{,}003{,}021x^2$ (J. Baumann, *Zeit. Verein f. Rüben. Ind.*, 1892, 824).

The method for determining dextrin in the presence of dextrose and maltose, by the action of mercuric cyanide as proposed by Wiley, has been reviewed by treating each of the substances separately with mercuric cyanide in alkaline solution. It was found that when the action was continued two minutes, the rotatory power of the dextrose was destroyed and that of the maltose much reduced, but that of the dextrin was also perceptibly diminished; which would indicate that the method was not wholly reliable (J. A. Wilson, Chem. News, lxv., 169).

For the determination of sucrose, dextrose, and levulose in mixture, an ingenious combination of gravimetric and optical operations has been proposed, which, according to the author's results, is reliable. A solution is carefully prepared, and its density and rotatory power determined; in a weighed portion the amount of reducing sugar is determined with Fehling's solution gravimetrically: another weighed portion is inverted, and the total reducing sugar in it determined. From the data thus obtained, viz., rotation and reducing sugar before and after inversion, can be calculated, by algebraic formulæ, the amounts of each of the sugars present. The original paper must be consulted for details (F. G. Wiechmann, *School of Mines Quarterly*, xiii., No. 3; Chem. News, lxvi., 237.

Formulæ for the determination of sucrose and raffinose in mixtures are proposed as follows:—$S = K_1A + K_2B$ and $R = K_3A - K_4B$, in which A and B are the direct and indirect polarisations of normal weights, and $K_1$, $K_2$, $K_3$, and $K_4$ are temperature coefficients (Mehay, "Sucrerie Ind. et Coloniale," *Chem. Centralbl.*, 1892, i. 508).

For the determination of starch a new method depends upon (1) the solubility of starch when heated with salicylic or benzoic acid; (2) the rotation of polarised light by such a starch solution; and (3) the fact that rotation is proportional to the quantity of starch. A weighed quantity of starch (2·688 grms. for Laurent's polariscope) is boiled with 80—90 c.c. water and 0·4—0·5 grm. of salicylic acid forty to fifty minutes, filled to a volume of 200 c.c. with addition of ammonia, filtered, and polarised in 400 m.m. tube. The reading of circular degrees corresponds to percentages. The method may be applied to commercial starch or potatoes, or similar materials (A. Baudry, *Chem. Centralbl.*, 1892, i., 339 and 509).

Another method for determining starch is to invert with dilute nitric acid and polarise the solution; in the case of cellular tissues the starch must first be extracted by boiling with oxalic acid, and then inverted with nitric acid (Guichard, *Bull. Soc. Chim. de Paris*, [3], vii., 554).

### *Heat Values, &c.*

The researches of Stohmann and Langbein upon the heat values of the carbohydrates, which have been extended over considerable time, is now well completed. Their work is of high character, but too extended for details in this space. As a general result they find that isomers give approximately the same values, and for homologous series the different members have a fairly constant difference. The heat value of the pentoses is about 560 calories; the methyl-pentoses, 711—718 cal.; hexoses, 672 cal.; disaccharides, 1351·5 cal.; and the polysaccharides (starch, &c.), 677·75 cal. (*Journ. Prakt. Chem.* [2], xlv., 305.

In the same way the study of the higher alcohols shows that for each addition of $CH_2O$ in the homologous series, there is a constant increase of 113 cal., which holds true of the synthetic gluco-heptit when compared with mannit (J. Fogh, *Compt. Rend.*, cxiv., 920.

## THE ANALYSIS OF IRON AND STEEL.[*]

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

(Concluded from p. 296).

### *Chromium.*

A satisfactory method for the determination of chromium has yet to be devised. In the methods generally employed the iron or steel is dissolved in the usual acids, the silica separated by filtration, and the chromium, together with the iron, precipitated in the filtrate by ammonia. After washing and drying, the precipitate is mixed, contained in a platinum crucible, with five times its weight of equal portions of sodium carbonate and potassium nitrate, and fused; the cold fused mass treated with water, the insoluble oxide of iron separated, and the filtrate acidulated with hydrochloric acid, mixed with a slight excess of alcohol, and boiled, whereby the alkaline chromate is reduced. After expelling the excess of alcohol a slight excess of ammonia is added, the solution boiled, the resulting chromium hydrate filtered off, washed, ignited, and weighed as oxide of chromium, ($Cr_2O_3$), which contains 68·62 per cent of chromium. Another method is to convert the chromium, contained in a solution as peroxide, into chromic acid, by passing a current of chlorine gas through, after nearly neutralising with sodium carbonate and adding an excess of sodium acetate. Upon boiling, the excess of chlorine is driven off and the iron precipitated, the latter being separated by filtration. The chromic acid in the filtrate is then reduced with alcohol and hydrochloric acid, the chromium precipitated as hydrate with ammonia, and weighed as oxide. Instead of precipitation as hydrate with ammonia, it may be thrown down as lead chromate by the addition of lead acetate.

The methods in which the solution remaining after the separation of the silica is employed for the determination of the chromium, do not furnish accurate results, as in the majority of instances a portion of the silica obtained invariably contains an insoluble phosphate, which carries a portion of the chromium along with it. This is especially the case with specimens containing notable quantities of phosphorus.

Another method, which in our experience has given very good results, is as follows:—One or two grms. of the metal, according to the amount of the chromium presumably present, contained in a beaker, is dissolved in 40 to 50 c.c. of hydrochloric acid, and the solution gently evaporated to dryness, the employment of an excessive heat being carefully guarded against. The cakey mass of chlorides is now broken up as completely as possible and removed to a porcelain dish, while the portions still adhering to the containing vessel are dissolved in a few drops of hydrochloric acid, the resulting solution rinsed into a platinum crucible with the least possible quantity of wash water, and the whole evaporated to dryness. To the contents of the platinum crucible, when dry, add the mass of chlorides contained in the porcelain dish, and intimately mix the whole with five times its weight of a fusion mixture composed of equal weights of sodium carbonate and potassium nitrate.[†] Place a cover on the crucible and fuse, employing at first a gentle heat, but gradually increasing to bright redness, for half an hour, whereby the oxide of chromium is converted into alkaline chromate. When cold the crucible is placed in a porcelain dish, covered with water, and heated until the fused mass is completely detached, when, after washing, it is withdrawn. The resulting solution is mixed with a few drops of alcohol, heated to boiling for an hour or so to reduce any alkaline manganate present, and allowed to stand until the oxide of iron has settled. Separate the oxide of iron by filtration through a double Swedish filter,[*] and wash the filter well with hot water. The filtrate is now acidulated with hydrochloric acid, excess of alcohol added, and the solution boiled; this results in the reduction of the alkaline chromate. The boiling is continued until the whole of the alcohol is expelled, and, when this is effected, to the solution add the slightest possible excess of ammonia, and digest at a gentle heat until the supernatant liquid is colourless. Collect the resulting precipitate, chromium hydrate, and filter; wash well, dry, ignite, and weigh as oxide of chromium ($Cr_2O_3$), containing 68·62 per cent of chromium.

In the Chemical News some time ago Messrs. Arnold and Hardy described a method in which the chromium is precipitated as a phosphate by means of sodium phosphate. The authors dispense with the filtering off of the iron oxide by taking a portion of the clear extract of the fusion equivalent to a known weight of the metal. They also condemn the employment of alcohol for reducing the chromate, and further state that it is not essential.

In steel, chromium may be very easily estimated by Galbraith's volumetric method. Two or three grms. are dissolved in dilute sulphuric acid (1 to $6H_2O$), after complete solution add crystals of potassium permanganate in somewhat slight excess, boil quickly until the pink colour disappears, and, if considered necessary, a few more crystals, and again boil; filter from precipitated manganese oxide. The filtrate contains the chromium as chromic acid. Add a weighed quantity of ferrous sulphate, "or, better, dissolve pure iron in dilute sulphuric acid and add to filtrate." Then determine the excess of iron unoxidised with standard bichromate solution. This quantity, deducted from the total amount used, equals iron oxidised by the chromic acid, which, multiplied by 0·3101 = chromium in the metal.

*Example.*—Two grms. of steel dissolved in HCl, 0·50 grm. pure iron added to solution iron unoxidised 0·175 grm.—

$$\frac{0·50 - 0·175 \times 0·3101}{2} = 1·52970 \text{ chromium.}$$

This method is accurate, and, in our own experience, very reliable.

Small quantities of chromium may be estimated by comparing the green colour of a solution containing the metal in the form of $CrO_3$ with a standard solution containing a known quantity of chromium. It is well known that chromium considerably modifies the value of steel, and at the present moment it seems desirable to occasionally test steels for this element.

### *Phosphorus.*

As regards the determination of this constituent many so-called "rapid" methods have been published, but we are not aware of one that really has any advantage, either for rapidity or simplicity, over the one we described in our first article. Usually the percentage of phosphorus in iron varies directly with the character and kind of ore used. Variations in blast-furnace working, leading to irregular reduction of silica and sulphur, appear to have little or no effect on the phosphorus contained in the ore, the whole of which practically passes into the iron, unless a very crude or white iron is made; in the latter case some proportion of the phosphorus passes into the slag.

### *Calcium, Magnesium, Aluminium, Nickel, and Cobalt.*

Aluminium, calcium, and magnesium are sometimes given in the analysis of iron and steel, but they are seldom looked for, with the exception of aluminium, which has recently been added to fused malleable iron and steel in small quantities, and is said to improve its quality, as also to facilitate the casting of the metal by

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[*] From *Industries.*

[†] If the solution and evaporation be effected in the platinum crucible, this will be unnecessary.

[*] Necessary on account of the fine state of division in which the oxide of iron exists.

lowering the fusing points, thus rendering it more fluid, producing sound malleable iron castings very free from honeycomb and blow-holes. This, however, has been questioned.

Calcium and magnesium may be determined by first freeing the original acid solution of the metal from iron, aluminium, and manganese, as previously described, evaporating the resulting filtrate to a very small bulk, exercising extreme care to avoid dust, &c. (apt to contain both calcium and magnesium), rendering alkaline with ammonia, precipitating the calcium by means of ammonium oxalate, and boiling. The solution is filtered through a Swedish filter, thoroughly washed, transferred to a crucible, and the precipitate converted by ignition at a white heat into calcium oxide, CaO, in which state it is weighed. CaO contains 71·43 per cent of calcium (Ca).

To the filtrate remaining from the precipitation of the calcium, contained in a porcelain dish, add some nitric acid, evaporate to dryness, and heat strongly. Repeat this operation two or three times, finally dissolve the dry residue in water, filter if necessary, add to the solution a little ammonium chloride, make ammoniacal,* add excess of ammonium phosphate, agitate the containing vessel well, and allow to stand in the cold for twenty-four hours. Collect the resulting precipitate of ammonium-magnesium-phosphate on a Swedish filter, wash with water containing ammonia, detach as completely as possible from filter-paper, ignite, add filter-ash, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$, containing 21·62 per cent of magnesium.

### *Determination of Aluminium.*

The iron and alumina are precipitated together by ammonia and ammonium acetate, from an acid solution of the metal, as in the determination of manganese, the precipitate transferred to a silver dish, and boiled for some time with a strong solution of pure caustic potash, the insoluble portion filtered off, thoroughly washed with hot water, and to the filtrate hydrochloric acid is carefully added until the precipitate alumina formed is re-dissolved. Neutralise the solution, which must be only slightly, but at the same time distinctly, acid with ammonia, and precipitate the alumina with ammonium carbonate, heat to boiling, collect the resulting precipitate on a filter, copiously wash with water until free from alkali, ignite, and weigh as alumina ($Al_2O_3$), which contains 53·40 per cent of Al.

As great difficulty is experienced in washing out the alkali, it is advisable to dissolve the $Al_2O_3$, after weighing, and re-precipitate. This method is not suitable for the determination of small quantities of alumina. A better method is to partly reduce the iron to the ferrous state (FeO); on treating as above $Al_2O_3$ is completely precipitated, together with a small excess of $Fe_2O_3$, and the alumina is thus more easily separated on boiling with potash. Or, if the amount of $Fe_2O_3$ be very small, this latter can be estimated by the colorimetric method, and deducted from the total weight of $Fe_2O_3$ and $Al_2O_3$ previously weighed. Or, the well-known method of Stead's may be used in lieu of the methods given; but in our practice we find the second of the foregoing to be sufficiently accurate.

The quantity of nickel and cobalt contained in iron and steel are, as a rule, very small. For the determination of the metals, the filtrate remaining after the separation of the silicon, as previously described, is diluted to a large volume, cooled, made neutral with sodium carbonate, the iron precipitated by the addition of a *large excess* of sodium acetate, the solution boiled for some time, and the basic acetate of iron filtered off. According to Crookes, the whole of the nickel and cobalt will be contained in the filtrate. It is, however, advisable to dissolve the iron precipitate in hydrochloric acid, and, after diluting largely and cooling, to neutralise with sodium carbonate, re-precipitate the iron with sodium acetate, boil, and filter, adding the filtrate to that remaining from the first precipitation. The volume of these mixed filtrates is considerably reduced by evaporation, after which it is made ammoniacal, ammonium sulphide added, the mouth of the containing vessel closed, and allowed to stand in a warm place for twenty-four hours.

The resulting precipitate of nickel, cobalt, and perhaps manganese, sulphides, are collected, digested in acetic acid to dissolve the manganese sulphide, and the residual sulphides washed, dried, and weighed. (For the method of separating the two metals, which is very complicated, see Dittmar's "Quan. Chem. Analysis," pp. 106 to 111.)

The methods herein described for the determination of chromium, titanium, arsenic, tungsten, &c., although the simplest and most rapid known to us, in a measure fail to meet the wants of the steel or ironworks' chemist, as, on account of the time consumed, regular daily determinations, as in the case of silicon, carbon, sulphur, &c., cannot be made. Naturally the steel-works' chemist rarely looks for these constituents, although it is very probable that these may often be present in iron and steel. Therefore the opportunities are few of comparing such analyses with the working of the metal, of fixing any limit as regards the maximum quantities of these allowable in steel or iron, or of determining to what degree the behaviour of the metal is affected when these are present in varying proportions.

Such methods would undoubtedly prove of incalculable value, but unfortunately they have yet to be devised, and until they are we are afraid the determination of the titanium, chromium, &c., as generally performed, will not prove of much real use.

## THE CHEMICO-LEGAL EXAMINATION OF STAINS SUSPECTED AS CONTAINING BLOOD.

By H. STRUVE.

It was not my purpose to give an opinion on the chemico-legal examination of suspected blood spots, since I am at present engaged with the collation of my nearly twenty-five years' experience as expert for judicial chemistry to the Caucasian Civil Medical authorities—a task which will still engage me for some months. If I, nevertheless, enter upon this question my inducement lies in Prof. G. Janecek's pamphlet on the limits of scope of the spectrum of hæmatin and the hæmine crystals as evidence of the presence of blood.

On the observations and facts recorded by Janecek, I must simply declare that he has attributed to slight, unimportant, and, in part, incorrect, observations a weight in the chemico-legal decision on blood spots which they by no means deserve. This reply would be somewhat short and condemnatory, and therefore not demonstrative and convincing. On this account I think it justifiable to deal more in detail with the facts communicated by Janecek.

The chemico-legal diagnosis of suspicious spots as to the presence of blood is often submitted by the Courts to experts,* both as regards spots which are without doubt occasioned by blood, and of such minuteness as to be merely recognised with the lens. In such cases, the judges in most cases call for a definite reply to the three following questions:—

1. Are the suspected spots due to blood?

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* A little tartaric or citric acid should be added to the solution previous to the addition of the ammonia and ammonium phosphate, to prevent the precipitation of any iron or alumina accidentally present.

* We believe that in Russia experts are not "called" respectively for the prosecution and the defence, but are consulted by the Courts. —*Ed.* C. N.

2. If to blood, is it human blood, or the blood of some other animal?

3. If blood is present, how old is the spot?

These three questions are the most usual, and to them the expert, according to the present state of our knowledge, can only reply that the spots submitted for examination are really blood spots or not; if blood, whether it has come from mammals, birds, or fishes. He cannot and must not go further, since we have not sufficiently well-founded facts for a certain diagnosis of the blood of different mammalia to admit of a definite reply, and conjectures and probabilities are here inadmissible.

The limits of the diagnosis of blood spots are clearly defined. The expert in his decision must remain purely objective, and leave all further inferences to the judges.*

The expert must uphold the results of his investigations with calmness and confidence; he has then fulfilled his task.

Among the blood stains which are laid before the expert for decision there belong those small spots which are often encountered on linen, clothing, and other objects. They are to be regarded as produced by the excretions of those parasitical animals which more or less frequently beset and annoy human beings, especially the lowest classes. These spots are very characteristically distinguished by their outward aspect, and can scarcely be mistaken for true blood spots. Among such stains we might include the dirt-spots of the common house fly, especially as, on suitable treatment, they display, according to Janecek, not merely the spectrum of hæmatin and of reduced hæmatin with a quite peculiar intensity, but readily give hæmine crystals.

Janecek assumes a peculiar blood-pigment in the excrements of flies, and hints at its possible connection with the myohæmatin found by McMunn in the muscles of invertebrates, and especially of insects. These facts completely clash with my experience. Years ago I undertook a series of experiments to which I was led by the phenomenon that if a fly is crushed a red spot is frequently obtained, occasioned by the colouring-matter of the eyes. I was particularly interested by this pigment, but on treating it with sodium chloride and acetic acid no crystals of hæmine were obtained. Other parts of the bodies of flies were often examined in the same manner, but there was no trace of crystals.

Not only flies, but spiders, were taken in hand, which had partly been fed for months under glass bells and had partly lived at large in the room. Their excreta were collected in sufficient quantity; it was not found possible to obtain from them crystals of hæmine, but the reactions of uric acid succeeded beautifully.

These experiments were concluded, laid aside, and forgotten, but were revived on reading Janecek's memoir. Still they were not decisive enough for the basis of my opinion. For this reason I used the opportunity, when spending this summer in Tiflis, in spite of the unusual heat and of the cholera epidemic, to make a further series of experiments relative to this question,

There was an excessive quantity of flies,† so that I could observe them as regards their diet and their excreta even more than was either necessary or pleasant. It appeared that the fly dirt was always modified by the substances which the flies had obtained for food. This was especially distinct with foods distinguished by a characteristic colour. If solutions of magenta, methylene-blue, or eosine were introduced into their food, these colours could be more or less distinctly recognised in the excreta even with a lens. Aniline ink was not rejected by the flies, as they are not select in their diet. If saccharine juices were offered them the excreta were adhesive, their colour was brownish, and the presence of sugar was detected in them by means of Fehling's reaction. If flies were fed with solutions of blood, the excreta were darker, of a brownish red, and minute portions, if heated in the usual manner with sodium chloride and glacial acetic acid, showed the characteristic crystals of hæmine. All attempts to detect uric acid in these excreta gave negative results.

From these observations I conclude that blood pigment can be found in the excreta of flies only if they have had the opportunity of feeding on blood, but not otherwise.

I was still not content with these experiments, but wished to convince myself in general whether flies contain a pigment which may be even approximately compared in its properties to blood pigment.

In order to obtain the necessary material, a number of dead flies, more or less thoroughly desiccated, were treated in a glass flask with alcohol (70 per cent) at the temperature of a dwelling room. The alcohol gradually assumed a faint yellowish colour; it was filtered off and submitted to distillation. This extraction was repeated until it no longer became visibly coloured. On distillation, the extracts appeared more decidedly yellow, but on spectroscopic examination no absorption bands were recognised.

The residual flies were then shaken out with ammoniacal alcohol. There ensued very slowly a more decided colouration of the solution, which gradually became stronger. Nevertheless, such solutions, even when concentrated by distillation, showed no absorption bands. On further evaporation, such solutions became turbid from small particles of fat, which could be afterwards removed by shaking out with ether. The residual aqueous solution had a brownish colour, and an acid reaction. On complete evaporation they left a brown residue, soluble in water, which became carbonised at higher temperatures, leaving a rather sparingly combustible carbon. Chlorine, sulphuric acid, and alkalis could be detected in the ash, but lime, ferric oxide, and phosphoric acid were entirely absent. I have not been able to make a more complete examination of these extractive substances, partly from insufficiency of material, partly because it would have required too much time.

In conclusion, I add that if we call to mind that the blood pigments are partially soluble in alcohol at 70 per cent, but entirely in ammoniacal alcohol, and that such solutions on sufficient concentration are distinguished by characteristic absorption bands, we must infer that in the flies which I examined no pigments are present comparable in their properties with the well-known colouring-matters of the blood.—*Zeitschrift für Analytische Chemie.*

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## THE DETERMINATION OF BORON.

By HENRI MOISSAN.

At the outset of our researches on boron and its compounds, we were led to re-examine the different methods of determining boron. That which gave the best results and presented the most general applicability is the method of Gooch, founded upon the action of methylic alcohol upon boric acid. We have modified this process so as to render it more expeditious and to avoid the errors due to the evaporation of small quantities of boric acid.

### *Theory of the Determination.*

The boron must previously be brought to the state of boric acid. This can be most generally effected by treating the substance under examination in a sealed tube. The mixture of boric and nitric acids is introduced into a flask. The boric acid is conducted away by pure methylic alcohol, and the liquid mixture is condensed in a Bohemian glass. The vapours are absorbed in ammonia, which is added to the liquid in the Bohemian glass after distillation. The liquid is poured upon a known weight of pure hydrated lime, weighed previously in the anhy-

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* This prudent rule cannot be maintained under the English system of examination and cross-examination, which treats the expert as a partizan.—*Ed.* C. N.

† This observation refutes the assertion sometimes made, that flies leave any district on the outbreak of epidemics.—*Ed.* C. N.

drous condition, and contained in a platinum crucible. After remaining in contact for a quarter of an hour, it is evaporated on the water-bath at a temperature bordering upon 70°. It is then calcined, and weighed again as calcium borate. The increase of weight shows the boric anhydride. A simple calculation indicates the quantity of boron.

The evaporation on the water-bath is rather tedious, and requires to be carefully watched. The mass is then dried at a gradually increasing temperature, and the crucible is ignited before the blast, at first covered with its lid and then open. The refrigeration is effected over quicklime in a desiccator.

The lime employed in this process must be prepared in the crucible itself, and in a special manner. Pure calcium nitrate is ignited so as not to effect entire decomposition and to produce a basic nitrate easy to manipulate and to preserve. This compound is converted into quicklime by strong ignition when required. It is necessary to ascertain that the crucible contains nothing but quicklime, which is known by the constancy of its weight after several ignitions. A large excess of lime must be used. To 0·5 grm. boric acid the author's crucible contained from 8 to 10 grms. of lime.—*Comptes Rendus.*

# RESEARCHES ON COBALT.

By HUGO REMMLER.

**The** author studies the question whether metallic cobalt purified according to the ordinary methods, is a unitary body?

Induced by the observation that, contrary to the statements of the text-books, aqueous ammonia has a solvent action upon recently precipitated cobalt hydroxide, the author has endeavoured to bring carefully purified cobalt material into solution by the slow fractionated action of ammonia upon cobalt hydroxide, and to determine the atomic weights of the metals found present in the successive solutions.

The author was especially concerned to establish, by means of an extended and connected series of experiments, whether the material used for the determination of atomic weights—or at least a part of it—was absolutely homogeneous; that is to say, whether all the fractions of the material, or a larger number of successive fractions, had the same combining weight for the element in question.

From 1200 grms. cobaltous chloride, dissolved in water, cobalt hydroxide was precipitated by means of bromine water and potassa-lye. It was freed from every trace of potassium chloride by careful decantation and washing. The cobalt hydroxide was precipitated in two flasks, and the entire mass was treated with 10 litres of ammonia, being frequently shaken. In this manner 25 ammoniacal extracts were obtained.

The residues, on evaporating down these extracts, were all worked up in exactly the same manner. They were dissolved in hydrochloric acid precipitated with hydrogen sulphide, and after filtration they were precipitated with ammonium sulphide from an ammoniacal solution in presence of ammonium chloride.

The sulphides thus obtained were treated with 4 per cent, and afterwards with 7 per cent, hydrochloric acid, until the iron reaction disappeared, and were finally dissolved in aqua-regia. After neutralising with potassa-lye and acidifying with acetic acid, the cobalt was precipitated with potassium chloride and sodium nitrite. The cobalt salt was again subjected to the purification just described by solution in aqua-regia, treatment with hydrogen sulphide, precipitation with ammonium sulphide, and washing the sulphide with hydrochloric acid. Lastly, the cobalt sulphide was dissolved in aqua-regia, the solution evaporated down, the residue taken up in water, the liquid freed from sulphur by filtration, and evaporated down with an excess of ammonia in order to convert any sulphuric acid into ammonium sulphate. The residue was ignited, and the cobalto-cobaltic oxide obtained was three times dissolved in hydrochloric acid, evaporated down with excess of ammonia, and ignited. Finally, the cobaltous chloride was converted into cobalto-cobaltic oxide by evaporation with nitric acid and ignition, and this was then submitted to examination.

The method which the author used for the determination of the atomic weight was essentially that pursued by Russell (*Journ. Chem. Soc.* [2], 1, 51), and afterwards by Zimmermann (*Liebig's Annalen*, 232, 394).

In it the cobalt oxides, formed by the ignition of cobalt compounds in the air, are first converted into cobaltous oxide by ignition in indifferent gases, and the latter is then reduced to metal by means of hydrogen. From the loss of weight of the substance used on the reduction of the cobaltous oxide to metallic cobalt, there results the atomic weight of the metal referred to oxygen ($O=16$).

The first seven extracts were made with ammonia of different strengths and different durations of action; the extracts 8 to 25 were obtained by treatment with ammonia of sp. gr. 0·960; the digestion in 8, 9, and 10 being carried on, is each for eight days, and in the remaining extracts for ten days each. The determination of the fractions thus obtained yielded the following values for the atomic weight of cobalt:—

| Fraction. | Atomic weight. |
|---|---|
| 2 | 59·53 |
| 3 | 58·79 |
| 4 | 58·92 |
| 5 | 58·78 |
| 6 | 58·72 |
| 7 | 58·67 |
| 8 | 58·38 |
| 9 | 58·48 |
| 10 | 58·30 |
| 11 | 58·37 |
| 12 | 58·60 |
| 13 | 58·51 |
| 14 | 58·65 |
| 15 | 58·83 |
| 16 | 58·79 |
| 17 | 58·86 |
| 18 | 58·52 |
| 19 | 58·53 |
| 20 | 58·65 |
| 21 | 58·77 |
| 22 | 58·78 |
| 23 | 58·44 |
| 24 | 58·53 |
| 25 | 58·48 |

To check the accuracy of the determinations of the atomic weights of the twenty-four cobalt proportions, the atomic weights of three fractions selected at hazard were determined in duplicate, whereby results were obtained which differed from each other at most only in the second decimal places.

No determination of the atomic weight of fraction No. 1 was made, as the quantity of cobalto-cobaltic oxide obtained was too small.

From the above table it is apparent that the cobalt metals occurring in the different fractions between 58·9 and 58·3, and their difference according to the check experiments, cannot be due to analytical error.

The author gives various causes for the striking phenomenon that from the 2nd to the 10th fraction the values decrease, and then from fraction 10 to 18 or 19 increase with tolerable regularity, and then again become smaller.

Since the material, as it appears from the investigation, is *not* homogeneous, the hydroxide may be attacked by ammonia differently, according to differences of temperature such as occur in the course of a year. In a mixture of two hydroxides, *one* constituent may have a different solubility in the solvent used than in a solution of the second constituent in the same solvent.

The author arrives consequently at the same conclusion as Gerhardt Krüss and F. W. Schmidt, that cobalt carefully purified by known methods is not a unitary substance. — *Zeit. Anorgan. Chemie*, ii., 442; *Zeit. Anal. Chemie*, xxxii., 273.

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## IRON AND ALUMINIUM IN BONE-BLACK: THEIR QUANTITATIVE DETERMINATION.

By Dr. F. G. WIECHMANN, Columbia College, New York.

THE determination of iron and aluminium in bone-black has thus far been commonly effected by the so-called ammonia-acetate method, which, until quite recently, has also been the favourite method employed for the determination of the constituents mentioned in mineral phosphates.

As this method, however, is open to serious objections, it was decided to test its accuracy, and to compare the results obtained with those yielded, respectively, by the method of E. Glaser (*Zeitsch. Angew. Chemie*, 1889, p. 636) and by the combination of Glaser's method with that of A. Stutzer (*Zeitsch. Angew. Chemie*, 1890, p. 43), first suggested by R. Jones (*Chemiker Zeitung*, 1890, p. 269) for the analysis of fertilisers.

For valuable analytical work performed in this connection, the writer's thanks are due to his assistant, Mr. E. C. Brainerd.

The schemes of analysis used in this investigation are minutely given in the following directions:—

### *Method* I.—*Acetate of Ammonia Process.*

(This method is based on the solubility of calcium phosphate in acetic acid, and on the insolubility of the phosphates of iron and aluminium in this medium).

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 3·0 grms. 4. Dissolve in distilled water + 25 c.c. HCl (conc.), boiling gently for one hour. 5. Filter. 6. Wash residue on filter until the wash-water no longer reacts for Cl with $AgNO_3$. 7. Add excess of $BaCl_2$, boil till $BaSO_4$ is granular. 8. Filter. 9. Wash the $BaSO_4$ on the filter till no more reaction for Cl with $AgNO_3$. 10. To filtrate and wash-waters combined add $NH_4OH$ until the precipitate formed begins to appear permanent, and boil. 11. Then add acetic acid to pronounced acid reaction. 12. Filter. 13. Wash the precipitate well. 14. Dry, ignite, weigh. 15. Regard the precipitate as $FePO_4 + AlPO_4$, calculate to $Fe_2O_3 + Al_2O_3$, and so report.

### *Method* II.—*Glaser's Method.*

(In this process the calcium is removed from an alcoholic solution by means of sulphuric acid before the precipitation of the iron and aluminium is effected).

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 5·0 grms. 4. Dissolve in distilled $H_2O$ + 30 c.c. HCl (conc.) + 10 c.c. $HNO_3$ (conc.). 5. Make the solution up to 500 c.c. with distilled water. 6. Filter. 7. Of the filtrate take 100 c.c. (equal to 1·00 grm.), place in a 250 c.c. flask, add 25 c.c. $H_2SO_4$ (conc.). Shake frequently, and allow to stand for five minutes. 8. Add absolute ethyl alcohol, cool, fill up to the mark with alcohol, and shake well. 9. As volume contraction will take place, fill up to the mark repeatedly with alcohol, and shake each time. Continue this filling up to the mark until no more contraction takes place. 10. Allow the solution to stand for twelve hours. 11. Filter. 12. Of the filtrate take 100 c.c. (=0·4 grm.), place in a large platinum dish on a water-bath, and heat until all the alcohol is removed. 13. Wash the remaining solution into a beaker with 50 c.c. of distilled water. 14. Heat to boiling, and then remove the flame. 15. Add $NH_4OH$ very carefully to alkaline reaction. 16. Boil until the ammonia is completely expelled. 17. Filter. 18. Wash the precipitate thoroughly with boiling distilled water. 19. Dry, incinerate, weigh. 20. Regard the precipitate as $FePO_4 + AlPO_4$, calculate to $Fe_2O_3 + Al_2O_3$, and so report.

### *Method* III.—*Combination of the Methods of Glaser and Stutzer.*

(Stutzer's method consists essentially in precipitating the iron and aluminium, principally as phosphates, in a solution of ammonium acetate; treating this precipitate with a solution of ammonium molybdate to remove the phosphoric acid as phospho-ammonium molybdate; filtering out this precipitate, and in the resulting filtrate precipitating the iron and aluminium as hydrates, by ammonium hydrate; drying and igniting this precipitate, weighing it as $Fe_2O_3 + Al_2O_3$, and reporting it as such).

The following scheme, it is believed, offers all the advantages of both the Glaser and the Stutzer methods.

Proceed exactly as in Method II., up to and inclusive of section No. 18. Then continue as follows:—

1. Place filter and contents in a beaker which contains 150 c.c. molybdic solution* at a temperature of about 40° C. 2. Keep the mixture at a temperature of about 65° C. for from twelve to fifteen hours. 3. Filter out the precipitate. 4. Wash the precipitate thoroughly with $NH_4NO_3$ solution (1 : 10). 5. To filtrate add $NH_4OH$ till it is well alkaline. 6. Heat for two or three hours over a gentle flame, replacing any loss by evaporation by the addition of water and ammonic hydrate. 7. Filter out the precipitate. 8. Dissolve this precipitate from the filter with HCl. 9. Precipitate with $NH_4OH$, and boil out all free ammonia. 10. Filter. 11. Wash precipitate, dry, incinerate, and weigh. 12. Regard the precipitate as $Fe_2O_3 + Al_2O_3$, and so report.

The mixture on which these three methods were tested consisted of—

| | |
|---|---|
| Tri-calcic phosphate .. .. .. | 20·00 grms. |
| Aluminium sulphate .. .. .. | 0·10 ,, |
| Ferrous sulphate .. .. .. .. | 0·10 ,, |

These amounts of the sulphates of iron and aluminium corresponded to 0·67 per cent of $Fe_2O_3 + Al_2O_3$, as was ascertained by analysis.

The mixture was dissolved in $H_2O + HCl$, and made up to 500 c.c. 24·75 c.c. of this solution contain 1·00 grm. of the dry substance.

In method I., used 3·00 grms.; in Method II., 1·00 grm.; in Method III., used 1·00 grm. of the "dry substance" for analysis.

*Results of Analysis.*

| | | Method. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| | | Per cent. | Per cent. | Per cent. |
| $Fe_2O_3$ | Present .. .. | 0·67 | 0·67 | 0·67 |
| $+ Al_2O_3$ | Found .. .. | 0·56 | 0·60 | 0·63 |

Method I. has evidently yielded the least satisfactory result.

Examining into its merits, it is readily seen that this method, as previously stated, is open to several serious objections: phosphate of aluminium is quite soluble in an excess of acetic acid; the precipitate of the phosphates of iron and aluminium is very apt to carry with it some of the calcium salt; the precipitate of the iron and aluminium obtained is not necessarily pure normal orthophosphate; and, finally, there is a great risk of intro-

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* Dissolve 100 grms. molybdic acid in 40 grms., or 417 c.c. of ammonium hydrate (sp. gr. 0·96), and pour the solution thus obtained into 1500 grms., or 1250 c.c., of nitric acid (sp. gr. 1·20). Keep in a warm place for several days, decant the solution from any sediment and preserve in glass-stoppered vessel.

ducing an error in calculating the combined phosphates of iron and aluminium over to the sesquioxides.¶

The molecular masses of the compounds concerned are:—

$$\begin{aligned} \mathrm{FePO_4} &= 151 \\ \mathrm{AlPO_4} &= 122 \\ \mathrm{Fe_2O_3} &= 160 \\ \mathrm{Al_2O_3} &= 102 \end{aligned}$$

If the constituents, the iron and the aluminium phosphates, occur in the precipitate in the proportion of their respective molecular masses, *i.e.*, 151 : 122, no error will be committed in assigning to this precipitate of the mixed phosphates the formulæ ($\mathrm{FePO_4+AlPO_4}$), and calculating to $\mathrm{Fe_2O_3}$, as is shown by the following example. Assume the composition of the precipitate to be—

$$\begin{array}{l} \mathrm{FePO_4} = 0{\cdot}151 \\ \mathrm{AlPO_4} = 0{\cdot}122 \\ \hline \mathrm{FePO_4+AlPO_4} = 0{\cdot}273 \end{array}$$

Calculating the combined phosphates over to the combined oxides—

$$\begin{array}{c} 2(\mathrm{FePO_4+AlPO_4}) : (\mathrm{Fe_2O_3+Al_2O_3}) :: .273 : x \\ 546 \quad : \quad 262 \quad :: .273 : x \\ x = 0{\cdot}131 \\ i.e.,\ (\mathrm{Fe_2O_3+Al_2O_3}) = 0{\cdot}131 \end{array}$$

Calculating the $\mathrm{FePO_4}$ and the $\mathrm{AlPO_4}$ separately over to their respective oxide, and then adding them—

$$\begin{array}{l} 2\mathrm{FePO_4} : \mathrm{Fe_2O_3} :: 0{\cdot}151 : x \\ 302 \ : \ 160 \ :: 0{\cdot}151 : x \\ x = 0{\cdot}080\ \mathrm{Fe_2O_3} \\ 2\mathrm{AlPO_4} : \mathrm{Al_2O_3} :: 0{\cdot}122 : x \\ 244 \ : \ 102 \ :: 0{\cdot}122 : x \\ x = 0{\cdot}051\ \mathrm{Al_2O_3} \end{array}$$

$$\begin{array}{l} 0{\cdot}0800\ \mathrm{Fe_2O_3} \\ 0{\cdot}0510\ \mathrm{Al_2O_3} \\ \hline 0{\cdot}1310\ \mathrm{Fe_2O_3+Al_2O_3}, \end{array}$$

which is identical with the value previously obtained. If, however, the iron phosphate and the aluminium phosphate are present in a proportion different from the one assumed in the above example, the result obtained by calculating their combined weight to combined oxides is wrong. It will be too high or too low, accordingly as the iron or the aluminium phosphate predominates.

*Example.*—Assume that the combined phosphates weighed exactly the same as before = 0·273 grm.; but assume the composition of the precipitate to be—

$$\begin{array}{l} \mathrm{FePO_4} = 0{\cdot}219 \\ \mathrm{AlPO_4} = 0{\cdot}054 \\ \hline \qquad 0{\cdot}273 \end{array}$$

Calculating the combined phosphates over to the combined oxides, of course the same result as previously found will be obtained, namely, that—

$$\underset{(\mathrm{FePO_4+AlPO_4})}{0{\cdot}273} = \underset{(\mathrm{Fe_2O_3+Al_2O_3})}{0{\cdot}131}$$

But calculating the $\mathrm{FePO_4}$ and the $\mathrm{AlPO_4}$ separately to their respective oxide, there is found—

$$\begin{array}{lcl} \mathrm{FePO_4} & 0{\cdot}219 = 0{\cdot}1160 & \mathrm{Fe_2O_3} \\ \mathrm{AlPO_4} & 0{\cdot}054 = 0{\cdot}0225 & \mathrm{Al_2O_3} \\ \left.\begin{array}{c} \mathrm{FePO_4} \\ + \\ \mathrm{AlPO_4} \end{array}\right\} & \begin{array}{c} \overline{\qquad} \quad \overline{\qquad\quad} \\ 0{\cdot}273 = 0{\cdot}1385 \end{array} & \left\{\begin{array}{c} \mathrm{Fe_2O_3} \\ + \\ \mathrm{Al_2O_3} \end{array}\right. \end{array}$$

a higher result than obtained above.

If the composition of the same weight of the combined phosphates of iron and aluminium be assumed to consist of—

$$\begin{array}{l} \mathrm{FePO_4}\ 0{\cdot}054 \\ \mathrm{AlPO_4}\ 0{\cdot}219 \\ \hline \qquad 0{\cdot}273 \end{array}$$

there will result as before—

$$\underset{(\mathrm{FePO_4+AlPO_4})}{0{\cdot}273} = \underset{(\mathrm{Fe_2O_3+Al_2O_3})}{0{\cdot}131}$$

But,

$$\begin{array}{lcl} \mathrm{FePO_4} & 0{\cdot}054 = 0{\cdot}0286 & \mathrm{Fe_2O_3} \\ \mathrm{AlPO_4} & 0{\cdot}219 = 0{\cdot}0915 & \mathrm{Al_2O_3} \\ \left.\begin{array}{c} \mathrm{FePO_4} \\ + \\ \mathrm{AlPO_4} \end{array}\right\} & \begin{array}{c} \overline{\qquad} \quad \overline{\qquad\quad} \\ 0{\cdot}273 = 0{\cdot}1201 \end{array} & \left\{\begin{array}{c} \mathrm{Fe_2O_3} \\ + \\ \mathrm{Al_2O_3} \end{array}\right. \end{array}$$

a value considerably lower than obtained by the other method of calculation.

Method II. makes a much better showing than the preceding method. The chief objection to it is the error involved in weighing the iron and the aluminium as phosphates and calculating them to the oxides, as explained above.

This difficulty, however, could be obviated in the following manner:—

Proceed with the analysis exactly as directed, and weigh the iron and the aluminium as phosphates; then dissolve in $\mathrm{H_2SO_4}$; reduce the iron by means of zinc and platinum in a $\mathrm{H_2SO_4}$ solution; titrate with standardised $\mathrm{K_2Mn_2O_8}$ solution, and record the iron as $\mathrm{Fe_2O_3}$; calculate this to iron phosphate, $\mathrm{FePO_4}$; subtract this value from the weight of the combined phosphates, and then calculate the remainder, the $\mathrm{AlPO_4}$ to $\mathrm{Al_2O_3}$.

Method III. has certainly yielded the most satisfactory result, for the difference between the amount of the iron and the aluminium oxides present and determined is only 0·04 per cent, a difference corresponding to less than two-tenths of a m.grm. in the actual weight of the precipitate, $\mathrm{Fe_2O_3+Al_2O_3}$, in this experiment.

The feature which serves as the special endorsement of this method is the fact that the constituents sought are reported in the very form in which they are weighed, and that thus the introduction of errors by calculation is excluded.

In order to test the working of these three methods in actual practice, they were applied to the analysis of four samples of bone-black.

The results obtained follow—

| Sample. | Method I. | Method II. | Method III. |
|---|---|---|---|
| 1 .. .. | 0·65 | 0·47 | 0·47 |
| 2 .. .. | 0·50 | 0·44 | 0·54 |
| 3 .. .. | 0·58 | 0·41 | 0·46 |
| 4 .. .. | 0·43 | 0·36 | 0·38 |

—*Science.*

**The Absorption of Hydrogen Selenide in Selenium Liquefied at a High Temperature.**—H. Pélabon.—It is known that if we heat in a sealed tube a mixture of selenium and hydrogen at a temperature above 250° and for a sufficient time, these bodies combine in part, yielding hydrogen selenide. If after thus heating a tube strongly charged with selenide it is allowed to cool in motionless air, the surface of the liquid selenium becomes the seat of an escape of gas and the liquid seems to boil. As the temperature falls the escape of gas becomes less easy, and, lastly, when the selenium arrives at the state of paste some bubbles burst the surface, projecting a little selenium outwards. The gas absorbed under these conditions by liquid selenium contains large proportions of hydrogen selenide.—*Comptes Rendus*, cxvi., No. 23.

## ON NICKEL-STEEL ARMOUR.

By SERGIUS KERN, M.E., St. Petersburg.

Amongst the various types of armour-plate that are now seriously engaging the attention of artillerists is the nickel-steel plate.

The Olouchoff Steel Works, St. Petersburg, started the manufacture of such armour-plate. The first plate produced had a trial quite recently. A perfect success is reported; it behaved in the same manner as the best nickel-plate coming from the French "St. Chamond Works." All the shells rebounded after penetrating the plate to nearly the thickness of the same. The steel shells were fired from a 6-inch breech-loading gun of 35 calibres, and had an initial velocity of 2200 feet per second. The Olouchoff plate remained uninjured, and showed no cracks. It contained 3 per cent of nickel and 0·3 per cent of carbon; Siemens-Martin steel was used.

As the Olouchoff Works have no rolling-mills, the ingot cast was rolled into a plate 8 ft. × 8 ft. × 10 inches at the Government Kolpino Works, and sent back to the Olouchoff Works for hardening and tempering. This was successfully done by engineer Rzeshotarsky.

The first three shells fired were manufactured by the Poutiloff Works, St. Petersburg; they remained whole and showed no cracks. The last two shells fired were prepared by the Olouchoff Works; the heads remained in the plate, and the rear parts of the shells broke up into small fragments, which were scattered over the ground.

We must add that the Poutiloff shells contained chromium (about 2 per cent), and were manufactured by the Pfoltzer process.

## DETERMINATION OF PHOSPHORIC ACID.

By MM. A. VILLIERS and FR. BORG.

The instructions which are found in analytical treatises and in the numerous memoirs which have been published on the determination of ammonium molybdate are very contradictory.

According to some authors the composition of the molybdic precipitate is variable, and we cannot find the weight of phosphoric acid present in the specimen from the direct weight of the precipitate. It must be dissolved in ammonia and precipitated with magnesia mixture, so as to form ammonium magnesium phosphate. According to others the composition of the precipitate is constant, and it may be weighed directly.

We have endeavoured to fix the conditions necessary for obtaining exact results.

We used the reagent of Sonnenschein and Eggertz, prepared by dissolving 150 grms. of ammonium molybdate in luke-warm water, making the solution up to 1 litre with cold water, and pouring it into 1 litre of nitric acid of sp. gr. 1·2.

We suppose, firstly, the entire absence of alumina and iron. We add an excess of the reagent—about 100 c.c. to 0·1 grm. of phosphoric acid ($PO_5$). The precipitation should be effected in the cold below 15° (the precipitate formed at higher temperatures is very thin, and is apt to pass through the filters). It is also well, in order that the precipitate may deposit rapidly, not to mix the reagent at once with the solution, but to let the former run carefully down the side of the beaker, and not to stir the mixture until two hours have elapsed.

In a solution of sodium phosphate the precipitation is complete in the cold after four hours. In presence of a great number of salts the precipitation is retarded, but it becomes complete after a more prolonged contact in the cold, or after four hours' digestion at about 40°. The influence of potassium salts is of the same kind, and, contrary to what has been said, it never determines an increase of the weight of the precipitate in consequence of a partial substitution of potassium for ammonium. The retardation produced by these salts is very decided.

In all cases the precipitation may be regarded as complete by digesting a mixture prepared in the cold as above, for four hours at 40°.

A more prolonged digestion is a cause of error, in consequence of a precipitation of molybdic acid.

The precipitate is then washed by decantation and filtration with water containing one-twentieth of its volume of the molybdic reagent.

The washing must not be effected with pure water, as the precipitate then passes through the filter. It is dried with the filter for six hours in a flask with a wide mouth, which has been first weighed with the empty desiccated filter, and we ascertain that the result obtained in a second weighing is identical. The ammonium phosphomolybdate has a perfectly definite composition, 1 part containing 0·03728 phosphoric acid ($PO_5$).

The desiccation cannot be effected above 100°, as the paper begins to turn yellow.

Precipitation with ammonium molybdate is an excellent method for the direct determination of phosphoric acid, in the absence of iron and alumina, of silica, of organic matter such as tartaric acid, and of substances which may reduce molybdic acid, such as the iodides. The precipitation will be always complete after four hours' digestion at 40°. The precipitate will not contain an excess of molybdic acid if the digestion is not further prolonged.

In presence of *aluminium* and *iron* the phosphomolybdate may contain a notable proportion of these metals. If iron is abundant its presence is even indicated by the deeper colour.

We cannot here weigh the precipitate directly. If we re-dissolve in ammonia and precipitate with magnesia mixture (as it is recommended in most analytical manuals), we still do not get rid of iron and alumina. We obtain, on the contrary, very accurate results in the following manner:—

We effect the precipitation of the ammonium phosphomolybdate and the washing as above directed without seeking to draw the precipitate upon the filter; we then dissolve with ammonia the portion contained in the filter, causing the ammoniacal liquid to flow back upon the principal portion of the precipitate. Lastly, after complete solution, we add tartaric acid. We may thus acidify the liquid without re-precipitating the phosphomolybdate. We then render the liquid slightly alkaline with an excess of ammonia, and determine the phosphoric acid as in the ordinary manner by precipitation in the state of ammonium-magnesium phosphate. The iron and alumina remain completely in solution, thanks to the presence of tartaric acid.—*Comptes Rendus*, cxvi., p. 989.

**Detection of Nitrobenzene.**—J. Marpurgo (*Pharm. Post*).—The author puts in a small porcelain capsule two drops of liquefied carbolic acid, three drops of water, and a fragment of potassium hydroxide of the size of a pea. The mixture is carefully heated to boiling, and the aqueous liquid to be tested for nitrobenzene is added. After prolonged boiling there appears a crimson ring at the margin of the liquid. On adding a saturated solution of chloride of lime, this ring takes an emerald-green colour. To detect nitrobenzene in soap it is dissolved in water, mixed with an excess of milk of lime, extracted with ether, and the ethereal residue tested as above. For detecting nitrobenzene in oil of bitter almonds, the fact may be utilised that the latter, if heated with manganese peroxide and sulphuric acid, loses its specific odour and assumes transiently an unpleasant smell, which gradually disappears, whilst nitrobenzol retains its odour on similar treatment.

## NOTICES OF BOOKS.

*Agricultural Journal.* Published by the Department of Agriculture of the Cape Colony. Vol. vi. May 18th, 1893.

The Cape Agricultural Department is making a very vigorous effort to extend sound agricultural knowledge throughout the Colony. The Journal before us is one of the agencies employed for this purpose. We are glad to see from the "Editorial Note" that "political or personal remarks will be strictly excluded."

It is complained that in many districts crops have suffered from the drought during the earlier part of the year. Locusts have also proved very troublesome. We must therefore beg to call the attention of the Editor to the utilisation of the eggs of locusts as reported from Algeria. These eggs yield an oil valuable both for therapeutical and industrial uses.

Experiments have been made with different kinds of wheat, such as the Dakota, the Medea, and the Neapolitan. The great point in view has been resistance to rust. The results have been somewhat complicated by the circumstance that wheats which have escaped rust in one district have suffered severely in another. It is concluded that the better the soil has been cultivated, the less the crop suffers from rust.

On the important subject of manures the writers of the "Agricultural Journal" follow the example of M. G. Ville in placing lime on a level with potash, phosphoric acid, and nitrogen. It is possible that the soils of South Africa may be poorer in lime than those of Britain. Here, where lime is needed, it is added to the soil separately, and not in conjunction with other plant foods, save when it is applied in the form of superphosphate.

As regards the various guanos and other manures, we note that the analyses have been almost all executed by aliens. Our British examiners, we fear, are found unequal in practice to chemists trained on a different system.

Experiments are being made with the Australian "salt-bush," *Atriplex nummularia*, which seems to be eaten by stock in preference to the native African species, *A. halimus*, which in addition seeds less readily.

The introduction of the Australian species is chiefly due to Sir Ferdinand von Müller, the distinguished Government Botanist of Victoria, to whom South Africa is also indebted for the acclimatisation of the Eucalyptus, which is now springing up by thousands in what were formerly treeless wastes.

Vine growers will read with great interest the account of the satisfactory results obtained, both in Africa and Australia, by the use of pure ferments from the most famous French growths—Burgundies, Bordeaux, &c.

Over irrigation, according to a correspondent, has rendered some lands barren from the accumulation of saline matter. As a remedy the Editor recommends the cultivation of beet, mangolds, and asparagus, and especially of the Australian salt-bush.

Attention has been called to cool storage for fruit, in view of the successful results obtained in Australia and Tasmania. A room of 2000 cubic feet is kept cooled to an even temperature of 40° to 45° for two months, at 30s. per week, though the outside temperature was about 92°. In such a chamber oranges can be kept in excellent condition from eight to ten weeks. We feel a very warm interest in these experiments. The demand for fruit in England is almost unlimited, and we should all prefer African or Australian produce to that of America or of the European continent, especially as the former growths would come in at a time when the latter are out of season.

*The Hygienic Treatment of Domestic Sewage.* Peter Spence and Sons, Manchester Alum Works.

This pamphlet has for its subject the treatment of sewage by means of Spence's "alumino-ferric" cake. This material, a compound of aluminium and iron sulphate, has proved itself most effectual in the treatment of sewage; and on the small scale it may, as here recommended, be used without the co-operation of absorbent agents such as become necessary when certain kinds of industrial refuse are mixed with the domestic sewage.

The instructions for the size, shape, and position of the settling tanks are thoroughly sound. The importance of a free access of air and light is insisted upon on account of the demonstrated efficacy of light in destroying morbific microbia. It is sad that so simple a truth should have been neglected by the London County Council to the great loss of the metropolitan rate-payers.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 23, June 5, 1893.

**Researches on the Iron of Orifak.**—Henri Moissan.—In the specimens of this iron, which M. Daubrée has placed at our disposal, we have found in one sapphire, in three amorphous carbon, in two sprouting graphite, and in one ordinary graphite, but in none of them diamonds, whether black or transparent.

**Genesis of Natural Phosphates, especially those which have Derived their Phosphorus from Organised Beings.**—Armand Gautier.—It is experimentally established that at least a part of the tribasic calcium phosphate and of the bibasic (brushite) results from the action upon limestone of ammonium phosphates derived in turn from the bacterian destruction of nitrogenous and phosphoric organised substances.

**The Assay of Manganese Oxides by Hydrogen Peroxide.**—Adolphe Carnot.—This paper will be inserted in full.

**Organo-Metallic Compounds Belonging to the Aromatic Series.**—G. Perrier.—In a former memoir (*Comptes Rendus*, May 15, 1893) the author has shown that anhydrous aluminium chloride combines with certain aromatic substances, acetones, aceton-phenols, ethers, and phenols. He now purposes to show that this combination is likewise effected with the chlorides of acid. To this end he has experimented with benzoyl chloride and aluminium chloride. He has studied the action of the organo-metallic compound obtained with benzoyl chloride upon the hydrocarbons and the phenols, benzoyl-diphenyl, benzoyl-retene, benzoyl-naphthol-$\beta$, and other chlorides of acids and aluminium chloride.

**The Use of Vine Leaves as Cattle-Food.**—A. Muntz.—The author recommends the consumption of vine leaves, after vintage, as food for cattle. In the south of France sheep are turned into the vineyard, after vintage, to consume the leaves. According to the author this practice is not injurious if the wood is thoroughly ripened. The sheep do not seem to be injured by the solutions of copper which are sprinkled over vines to destroy fungi, &c.

Erratum.—P. 293, col. 1, line 2 from top, *for* "even" *read* "soon."

# INDEX.

END OF VOLUME LXVII.

# THE
# CHEMICAL NEWS

AND

## JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

*WILLIAM CROOKES, F.R.S., &c.*

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THE CHEMICAL NEWS.

VOLUME LXVIII.

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No. 1754.—JULY 7, 1893.

# ESTIMATION OF SOLIDS AND FAT IN MILK.

By JOHN BOYD KINNEAR.

THE observations of Messrs. Liebermann and Székely on the examination of milk, given in the CHEMICAL NEWS (vol. lxvii., p. 280), lead me to offer some remarks based on my own experience. Like these gentlemen (and many others) I have attempted to use the plan of direct solution of the fat in ether or petroleum spirit, and with very good success in samples tolerably rich in fat; but I have found that when the milk is very poor in fat, or is skimmed, the ether frequently assumes a gelatinous state. I do not know what may be the substance with which it unites in this combination, probably one of the albuminous compounds. It is not prevented by addition of salts of either mercury, copper, or lead; but I have found it in a great measure or entirely obviated by previous addition of carbolic acid. Unfortunately, however, the phenol itself is soluble in ether, and I have not ascertained whether it is wholly taken up by the ether, or whether part remains in the milk. This uncertainty prevents its use in quantitative analysis.

After many experiments I have come to adopt the following method for estimating accurately and rapidly the total solids and fat, and it has the advantage of being equally applicable to cream, or to rich or to skimmed milk:—On a piece of thin, flat-crown-glass, previously tared, and 2 or 2½ inches diameter, pour a few drops of the milk, and weigh. About a gramme is a convenient quantity, but a little more or less is immaterial. It is then dried, either in a hot-air chamber or by being held at a considerable height over the flame of a lamp. The film being so thin, this process requires only from five to ten minutes. Before being perfectly dry (but after it has become solid) it is well to raise or scrape the film from the glass by a steel scraper, for which purpose a knife or a sharp carpenter's chisel answers very well, placing the glass on a sheet of black glazed paper, and putting a guard of the same material in front of the scraper, to prevent any loss of particles of the hard cheesy matter. After this it can be very quickly brought to a constant weight, and being very slightly hygroscopic, the percentage weight of the "dry solids" can be determined with great accuracy to the second decimal point.

If the specific gravity of the milk has been previously ascertained, Fleischman's formula will give the percentage of fat from these data within 0·1 or 0·2 per cent. But to obtain it gravimetrically I transfer the dry solids to a small tared stoppered bottle, about ½-ounce size and rather tall, and pour upon them 3 or 4 c.c. of ether. The stopper being tied down, the bottle may be placed in warm water—from 100° to 120° F., according to the strength of the bottle—and left in it for a few minutes, then shaken up for another minute. The hot ether is a much more effective extractor of the fat than it is when below the boiling-point. After being cooled the bottle is weighed, and, deducting its own weight and that of the solids, we get the weight of the contained ether, which may be designated E. The stopper is now removed, and a portion (as much as possible) of the clear solution poured quickly into a small tared watch-glass, the stopper immediately replaced, and the bottle again weighed. The difference between this and the last weighing represents the ether plus fat in the watch-glass, which we will call $e+f$. On this being evaporated we obtain $f$ only, which is accurately weighed on the watch-glass, and gives us the weight of $e$ by difference. If we call the weight of the milk originally taken M, and the total fat it contained F, we get the proportion $e : E :: f : F$, from which

$$F = \frac{E \times f}{e},$$

and as the percentage of fat in the milk would be

$$\frac{100\,F}{M},$$

we get, as the formula for calculating the percentage,

$$\frac{100\,E \times f}{M \times e}.$$

The advantage of taking an aliquot part of the ethereal solution, which is the method recommended by Dragendorff in plant analysis, is that it saves the very tedious process of filtering and washing the filter with ether. The whole of the fat is really in the solution, just as it is in Soxhlet's aræometric method, and the sole possibility of error arises from the evaporation of the ether during the moment of pouring from the bottle into the watch-glass. To the extent of this loss the quantity estimated by difference on the watch-glass will be over the truth, and the milk will appear poorer in fat. A small correction by deducting, say, 50 m.grms. from $e$ in the divisor may be allowed for this. But an error of ±0·050 grm. in the ether taken, supposing that to be about three-fourths of the whole ether employed, will only amount to 0·06 per cent of fat in average milk, or to 0·01 per cent in skim milk, so that for practical purposes it is hardly worth attention. It would almost disappear if petroleum spirit were employed. The whole determination of solids and fat may by this method be completed in less than half an hour, and several samples may be examined simultaneously. An additional recommendation is the simplicity of the apparatus and the economy in the ether employed.

June 26, 1893.

## QUALITATIVE AND QUANTITATIVE ANALYSIS OF FORMALDEHYD.

By A. TRILLAT.

Since formaldehyd (the formol of commerce) is come into use as a material for the manufacture of certain dyes and as an antiseptic, it becomes important to know methods for detecting its presence and for determining its quantity in its solutions. The qualitative detection is effected as follows:—

On oxidising tetramethyldiamidodiphenylmethan by lead peroxide and acetic acid, there appears an intense blue colouration. I have utilised this reaction to detect the presence of formaldehyd in a solution in a free state, or, in certain cases, in combination. We pour half a c.c. of dimethylaniline into the solution in question, and stir briskly after having acidulated with a few drops of sulphuric acid. The combination between dimethylaniline and formaldehyd is easily effected by heating the mixture for half an hour on the water-bath. After having rendered it alkaline with soda, it is heated to ebullition until the odour of dimethylaniline has completely disappeared, when it is passed through a small paper filter. After washing, the filter is spread out at the bottom of a small porcelain capsule, moistened with acetic acid, and there is thrown upon it a small quantity of lead peroxide in fine powder. The blue colouration shows the presence of formic aldehyd.

### *Second Method.*

I have found that the formation of anhydroformaldehydaniline, $C_6H_5N : CH_2$, is very easily effected by causing formaldehyd to act upon aniline; not in presence of acids, but simply in a dilute aqueous solution. This aqueous solution of aniline is obtained by dissolving 3 grms. of aniline in 1 litre of distilled water. I mix 20 c.c. of this solution in a test-tube with 20 c.c. of the liquid in question, and neutralise. In presence of formic aldehyd there appears, after some hours, a very slight white cloud. This reaction is very sensitive, enabling formaldehyd to be detected in a solution at $\frac{1}{20000}$. In this case the turbidity appeared only after some days. The reaction is common to acetic aldehyd.

### *Detection of Formaldehyd in Alimentary Substances.*

The liquid products, after being decolourised and filtered, are submitted to one of the foregoing methods.

Solid products are treated with hot water, in order to dissolve trioxymethylene, which may be derived from the polymerisation of formaldehyd. A microscopic examination of the substance may give useful indications.

The detection of formaldehyd in alimentary substances is often impossible, because it forms with certain organic principles compounds from which it cannot be separated.

### *Determination of Formaldehyd.*

*First Method.*—A method has been proposed for determining formaldehyd which consists in estimating the quantity of ammonia necessary to transform it into hexamethylene. In this method we add to a solution of formaldehyd a known quantity of ammonia, and titrate the excess with sulphuric acid. This process is faulty, because the solutions of commercial formol have always a certain degree of acidity, and because hexamethyleneamine has an alkaline reaction, which the method overlooks. To avoid these causes of error I proceed as follows:—

I determine previously the acidity of a known quantity of the solution by means of normal soda, using phenolphthalein as indicator.

I measure 10 c.c. of the solution in question into a flask, dilute with water, and add a known quantity of a standard solution of ammonia until the odour is distinctly ammoniacal. The contents of the flask are then treated with a current of steam so as to expel the excess of ammonia, which is collected in water, and determined by means of a standard solution of sulphuric acid. We find the quantity of combined ammonia by deducting from the total quantity added that which is found in excess in the distillate, and taking account of the original acidity of the solution. The following equation enables us to calculate the proportion in which the combination takes place:—

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

In this process a small portion of the hexamethyleneamine is carried away in distillation.

*Second Method.*—To a solution of 3 grms. aniline in 1 litre of water we add, drop by drop, with constant agitation, from 1 to 4 c.c. of the solution in question, according to its suspected strength. There is formed a white cloud, which after repeated agitation is entirely deposited. After forty-eight hours the liquid is passed through a tared filter, and we ascertain that the filtrate contains an excess of aniline. We dry at 40°, and weigh. The corresponding quantity of formaldehyd is given by the equation—

$$C_6H_5NH_2 + CH_2O = C_6H_5N : CH_2 + H_2O.$$

By operating under these conditions, we obtain results strictly comparable; but the analysis of the anhydroformaldehydaniline does not give figures which exactly agree with the formula. Still, they approach it so closely as to be in most cases approximately satisfactory.—*Comptes Rendus*, cxvi., p. 891.

## GENERAL METHOD FOR THE ANALYSIS OF BUTTERS.

By RAOUL BRULLÉ.

The falsification of fatty substances has become extremely common, and the injury which it occasions to the dairy industry is so great that the public authorities and the agricultural societies and syndicates have been endeavouring to find means for the repression of the fraud.

Unfortunately, the substances used for sophistication are themselves so varied that it has been hitherto impossible to find a procedure sufficiently general to be applicable in all cases.

The foreign fatty matters added to butters are sometimes of animal origin (oleomargarine, grease, &c.), sometimes of vegetable origin (seed oils, olive oil, &c.).

All these different cases of falsification may be detected by a combination of reactions which I have learned in the course of a prolonged practice.

1. The presence of seed oils in butters is detected by the use of silver nitrate in an alcoholic solution, which gives very characteristic changes of colouration when there is a mixture. We heat 12 c.c. of butter in a test-tube with 5 c.c. of solution of silver nitrate at 25 per 1000. The microscopic examination of the crystals obtained on cooling enables us to detect adulteration with olive oil—the only one which would escape this test.

2. The detection of animal fats is more difficult. For this purpose we heat 5 c.c. of butter, previously melted and filtered, to 148° on the oil-bath. The butter is placed in a flat-bottomed capsule, 7 c.m. in diameter. When the substance has reached the temperature of 130° we add a pinch of powdered pumice and eight drops of fuming nitric acid. We mix, and heat for about twelve minutes; it is then set to cool in a place at 21°. After an hour, we proceed to the assay with the *oleogrammeter*. This instrument consists of a vertical rod surmounted by

a broad plate, and gliding in a ring fixed to a stand. The end of the rod is applied on the hardened surface of the refrigerated fatty matter. Weights are placed upon the plate until the point of the rod sinks abruptly into the substance. The weights represent the resistance of the butter under examination to the oleogrammeter. The results obtained are very surprising. In fact, if the sample is a pure butter, the penetration of the butter is effected with a mean load of 250 grms. The same experiment made with pure margarine requires 5000 grms. The intermediate figures enable us to estimate with sufficient accuracy the proportions of a mixture of margarine and butter. A weight of 900 to 1000 grms., *e.g.*, corresponds to a butter containing 10 per cent of margarine.

When the margarines contain considerable proportions of seed oils, the indications of the oleogrammeter present great deviations, but the use of silver nitrate enables us to overcome this difficulty, as the two methods are complementary to each other.—*Comptes Rendus*, cxvi., p. 1255.

## A NEW METHOD FOR REDUCING METALLIC OXIDES.*

By WM. H. GREENE and WM. H. WAHL.

In a previous paper by ourselves, presented at the January meeting of the Section, we gave an account of the various methods that have been proposed for the production of metallic manganese, and described a method which we had devised for the production of this metal, and which we believe to be adapted for commercial use, based on the reduction of one of the lower oxides of manganese by means of aluminium.

In the search for commercially available reducing agents applicable to the solution of the manganese problem we gave consideration to all the elements of which the known thermo-chemical data gave us reason to hope for an exothermic reaction with the oxides of manganese.

Among these silicon did not escape our observation, in asmuch as the heat of formation of its oxide $SiO_2$, according to the most reliable estimates, is sufficiently greater than that of $2MnO$ to permit us to expect that the desired reaction should take place.

The references in the literature of chemistry to the reducing action of silicon are not numerous. The only investigations that appear to have a direct bearing thereon are those of Gore,† who makes the observation that "crystals of silicon thrown upon melted argentic fluoride become red hot, undergo rapid combustion, forming fluoride of silicon and depositing silver." By adding crystals of silicon to melted black oxide of copper, the same author‡ observed a sudded incandescence which raised the temperature to full white heat; copper was also deposited and melted to a red metallic bead and could be hammered to a thin sheet. He noted also that crystals of silicon immersed in a solution of fluoride of copper, containing free hydrofluoric acid, instantly coat themselves with bright copper, and that when silicon is thrown into melted fluoride of sodium, bubbles of vapour are evolved which explode and burn with a yellow flame at the surface of the liquid. The silicon was found subsequently to have lost in weight.

More recently Warren (Chemical News, vol. xlv., 75) has published an account of a number of instructive experiments, which strikingly illustrate the energetic reducing properties of silicon. He notes the fact that metallic silicon, though a very stable and inert substance, yet when in admixture with a large number of metallic oxides, becomes at once oxidised, the oxide in admixture with the same becoming itself reduced. Litharge, for example, when mixed in excess with silicon and heated to dull redness, becomes reduced to metallic lead. With copper and all other readily reducible oxides, either a silicide, or, when the oxide is in excess, the pure metal, is obtained. He observes that even the oxides of chromium, tungsten, and molybdenum are reduced to the metallic state when heated with silicon.

The fact that silicon in the elementary form can only be obtained by indirect and costly methods rendered any serious consideration of its availability for our purpose out of the question. The thought presented itself, however, that compounds of silicon might possibly be found to answer our purpose, and a very slight consideration of the subject encouraged us to believe that in the metallic silicides we had at hand a ready means of utilising the chemical energy of one of the most powerful reducing agents.

It appeared reasonable to conclude, also, that the reducing power of such silicides might be found serviceable not only in the reduction of the oxides of manganese, but also in the reduction of many other metallic oxides.

Certain facts in connection with the metallurgy of steel and copper when given their proper interpretation appeared to strengthen this view. Thus, in one of the modifications of the open-hearth process of steel making, in which pig iron and scrap are melted on the hearth in contact with oxides of iron, not only the greater part of the carbon but also practically all of the silicon which is invariably present in small proportion is eliminated from the resulting steel, by the reaction with the oxides of iron, and finds its way into the slag as silicate.

Also, in the commercial operations of reduction, re-melting and casting of certain metals and alloys, serious practical difficulties arise from the formation or retention therein of small quantities of oxide which have an unfavourable influence upon the strength, ductility, and other desirable properties of the metals and alloys, and often render it troublesome to roll them or to obtain sound castings from them.

To counteract such difficulties, compounds in which silicon is present have come into use, either for the purpose of prevention or correction. We may refer as illustrations to the use of ferro-silicon in foundry practice and in the open-hearth process, and to the suggested use of copper, tin, and zinc silicides to copper, tin, and zinc and their alloys, all for the same general purpose of insuring the production of homogeneous metal and sound castings. In these cases the utility of the silicon appeared to us to be due manifestly to its energetic reducing action on the minute quantities of oxides retained in the molten metal, and to be strictly comparable to the action of phosphorus, magnesium, manganese, aluminium, and other energetic reducing agents employed in the purification or refining of metals from small quantities of retained oxides.

Having satisfied ourselves from preliminary considerations of this nature that the use of silicon in the form of the metallic silicides might hopefully be applied as the basis of a commercial method for the reduction of oxidised ores of the metals, we proceeded at the first opportunity to make a number of experiments to test the correctness of our reasoning.

The requirements of iron founders and steel makers, we found, had caused a considerable demand for pig irons containing relatively high proportions of silicon. These are known to the trade as ferro-silicon, silico-spiegel, and silico-ferro-manganese, the last two being so designated from their manganese content. These products may be described as silicides of iron, or of iron and manganese, containing from 5 to 30 per cent. of silicon, and a relatively low percentage of carbon. These silicides seemed adapted to our purpose.

We will confine ourselves here, for convenience, to the description of our method as applied to the production of ferro-alloys. It is obvious that in the production of such alloys, which, if useful at all, will find their principal

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* Read at the Chemical Section of the Franklin Institute, March 21, 1893.

† Chemical News, vol. xxix, 291.

‡ Gore, "The Art of Electro-metallurgy" (1877), p. 220.

application in the manufacture of special steels, the presence of carbon in notable proportion will be highly detrimental.

For this reason we require for our purpose a silicide containing as high a proportion of silicon and as low a proportion of carbon as possible. Silicon irons and spiegels containing as high as 15 per cent. or 20 per cent. of silicon, and with carbon not exceeding 1 per cent., can readily be obtained, and, as we are assured, by special selection of ores and fluxes, can be supplied on demand even higher in silicon than the figures just named. It is interesting also to note the fact that, as a rule, the quantity of carbon, in such silicides varies with the silicon in an inverse ratio, the carbon dacreasing as the silicon increases, and *vice versa*.

We may fully illustrate our method by describing its application to the production of a ferro-manganese; the object in view being substantially the manufacture directly from the oxide of a ferro-alloy sufficiently high in manganese and at the same time sufficiently low in carbon that it may be employed with economic advantage in the production of manganese steel, the deoxidation of the charge in the Bessemer converter, or on the open hearth.

The possible utility of the method may most strikingly be illustrated with reference to the ultimate production of manganese steel, an alloy that is known to possess certain unique and highly desirable qualities, but which presents certain practical difficulties in its manufacture in large quantities which thus far have proved to be troublesome.

By the way of explanation it should be stated that by the present method of manufacturing this alloy, which consists substantially in the addition of ordinary ferro-manganese to fluid iron, the proportion of manganese that can usefully be introduced into the steel is rigorously limited by the carbon, which to the amount of 5 to 6 per cent. is present in the ferro-manganese and which cannot be eliminated therefrom because of its affinity for manganese.

With this explanatory comment we proceed to describe the production of a ferro-manganese by the method which we propose. The chemistry of the operation is extremely simple. When a ferro-silicon (or other silicide) is heated in any suitable furnace chamber (which for our purpose is preferably lined with basic material, such as lime or magnesia) in contact with a metallic oxide (or a mixture of such oxides) and in the presence of a suitable base, such as lime, magnesia, or alumina, the oxygen of the oxides combines with the silicon, forming silica, which at once unites with the base to form a more or less fusible silicate that separates as slag, while the metals set free combine to form an alloy.

The mode of our procedure is, precisely stated, as follows:—We select a ferro-silicon or silico-spiegel adapted for our purpose, and melt the same on the hearth of a furnace or in a crucible. Then the manganese monoxide (or the protosesquioxide) with which a fluxing material has been incorporated is added in proper quantity. The reaction takes place promptly, the silicon of the ferro-silicon seizes upon the oxygen of the manganese ore, and is thereby converted into silicic oxide which forms with the flux a liquid slag, while the manganese set free by the reduction of the ore combines with the molten iron set free from the silicide. The whole charge of manganese and flux may be added to the ferro-silicon at once, or the addition may be made by portions until a sufficient quantity of the oxide has been employed to utilise the reducing power of all of the silicon that was present in the ferro-silicon, thus reducing a chemically equivalent quantity of manganese oxide to the metallic state.

Assuming that we operate with a silicide containing iron 88 per cent, silicon 10 per cent, carbon 1 per cent, the reaction for simplicity's sake may be supposed to take place according to the equation—

$$2MnO + Si = SiO_2 + 2Mn.$$

We would then employ silicide and manganese oxide in quantities that satisfy the above proportions, *i.e.*, for every 28 parts of silicon in the silicide 142 parts of manganese monoxide and a quantity of lime, manganese, or alumina, or a mixture of these that will completely combine with the silicate to form a fusible silicate.

It is necessary, of course, to use a larger quantity of manganese ore than that required by theory, for the reason that a certain quantity of the manganous oxide is always seized upon by the silica and passes into the slag in the form of manganous silicate.

A charge of ferro-silicon (containing 10 per cent silicon, 1 per cent carbon) 100 pounds, manganese monoxide 70 pounds, lime 50 pounds, we have found to yield about 128 pounds of a metallic alloy having the composition—Iron 70 per cent, manganese 29 per cent, carbon 0·7 per cent, silicon trace.

Assuming that the permissible percentage of carbon in a certain manganese steel is 0·5 per cent, then 100 pounds of a manganiferous alloy of the above composition will produce by mixture with 40 pounds of decarburised iron, 140 pounds of manganese steel of the composition—Iron 78·8, manganese 20·7, carbon 0·5, silicon trace.

In the preparation of a manganese steel containing the same percentage of carbon by melting decarburised iron with ordinary ferro-manganese containing 80 per cent manganese and 5·5 per cent carbon, the resulting metal would contain 92·23 per cent iron and only 7·27 per cent manganese. Or, making the comparison on the basis of equivalent quantities of manganese, the manganese steel made from the ordinary ferro-manganese would contain for 20·7 per cent manganese, 1·4 per cent carbon; that made by our process would contain for 7·27 per cent manganese only 0·18 per cent carbon.

In many cases it is obvious that a metal of the desired composition may be obtained directly by one operation on the furnace hearth. It is probable, for example, that for the production of a manganese steel of a given composition, the required proportions of scrap wrought iron and ferro-silicon of suitable composition could be melted on the hearth, in contact with the manganous oxide.

By procedures substantially like that described, but substituting for the manganous oxide, oxides of nickel, chromium, and tungsten, we have succeeded in forming ferro-alloys of nickel (containing as high as 50 per cent of this metal), chromium (with nearly 20 per cent of chromium), and tungsten (with more than 50 per cent of tungsten). With titanium we have thus far obtained only doubtful results. In all these cases the resulting ferro-alloy is relatively low in carbon, and, as the method we propose does not involve the introduction of carbon either as the reducing agent or from external sources, the carbon in the product being derived wholly from that which is contained in the ferro-silicon employed in the operation, we have reason to believe that we will be able to produce, on the commercial scale, ferro-alloys with any desired metals so low in carbon as to meet all the requirements of the metallurgical arts.

Thus far our experiments have been confined to the ferro-alloys and have been on the laboratory scale. It will be obvious, however, that the chemical reactions involved will hold good for other classes of alloys, and that alloys of copper, for example, with difficultly reducible metals, may be obtained quite as readily by fusing the appropriate oxides with copper silicide.

In conclusion, the method which we propose, we believe, will enable the metallurgist advantageously to effect the reduction of numerous metallic oxides without the employment of carbon, and the production of numerous useful and important alloys.

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On the Scission of Carbonic Acid in consequence of Solar Radiation. — A. Bach. — Very diffuse solar radiation, and even the light of a gas-flame, occasions the splitting up of carbonic acid in presence of dimethylaniline.—*Comptes Rendus*, cxvi., No. 24.

## THE DETECTION OF LEAD IN URINE.

By LEE K. FRANKEL, Ph.D.

During the winter of 1891-92 the author, while investigating some cases of supposed lead-poisoning, had occasion to require a method whereby lead could be accurately and, what was of equal importance, rapidly detected in the urine. As far as accuracy was concerned, the methods recommended by Victor Lehmann (*Zeitschrift für Physiologische Chemie*, vi., 1) were found to be thoroughly satisfactory, but it was hoped that a modification of his electrolytic method could be devised which would shorten the time limit of the process. Unfortunately, the desired end was not attained, since the results are altogether of a negative order. These, however, show a sufficiency of new and interesting data to warrant their publication.

In the article above referred to, Lehmann states that lead may be detected electrolytically in urine, either with or without previous destruction of the organic matter present there. The best results are given when the organic matter is first destroyed. He uses in his investigations the apparatus devised by Bloxam (*Chemical Society Quarterly Journal*, xiii., 12) for the electrolytic detection of arsenic. The apparatus consists essentially of a jar, which is closed below with parchment, and in which the solution to be examined is placed. The jar stands in an outer vessel which contains sulphuric acid. In Lehmann's apparatus, the platinum electrode which is attached to the negative pole of the battery dips in the outer vessel, while that attached to the positive pole enters the jar. He states that with such an arrangement the lead present in the urine deposits as peroxide on the positive pole.

To ascertain how minute the quantity of lead in a solution might be, and still show as peroxide when the solution was electrolysed, the author made the following determinations: In a platinum dish, connected with the negative pole of a battery, 100 cubic centimetres of water and 1 cubic centimetre of lead-nitrate solution were placed. To these 3 cubic centimetres of concentrated nitric acid were added. The positive electrode was now introduced directly into the solution, and the latter electrolysed with a current generating 1·4 cubic centimetres of oxyhydrogen gas per minute. At the end of 30 minutes the deposit of peroxide of lead on the platinum foil was already very distinct, and at the end of several hours had the usual dark brown appearance of the lead-peroxide deposit. The lead-nitrate solution used was of such a strength that in the solution finally electrolysed 1 part of lead was present in every 100,000 parts of water.

Two more experiments were made with solutions containing 1 part of lead to 500,000 and 1,000,000 parts of water respectively, the amounts of nitric acid and the strength of current being the same as in the preceding experiment. The deposits of lead peroxide on the platinum foil, while very faint, were still distinctly recognisable. The delicacy of this electrolytic test led the author to hope that the presence of urine would not materially interfere with the deposition of the peroxide of lead. The following experiments will, however, show that the results obtained were radically different from those which were anticipated from the above action of the lead solution.

To 100 cubic centimetres of urine 1 cubic centimetre of a lead-nitrate solution (containing about 1 m.grm. of lead) and 10 cubic centimetres of concentrated nitric acid were added. The solution was put into a platinum dish and electrolysed for 24 hours with a current generating 1·4 cubic centimetres of oxyhydrogen gas per minute. At the expiration of that time, to the author's surprise, no peroxide of lead had deposited on the positive electrode. The current was then allowed to act 48 hours longer; even then no disposition was noticeable on the positive pole, but on the platinum dish (the negative electrode) a metallic deposit resembling lead had formed. The quantity of the deposit, however, was so small that it did not respond to the ordinary tests for lead.

130 cubic centimetres of urine and 2 cubic centimetres of the lead-nitrate solution, the free nitric acid in this case being omitted, were similarly electrolysed, with the difference that in this determination the platinum dish was made the positive electrode and the platinum foil the negative electrode. After electrolysing for 24 hours with the same strength of current as before, a greyish-brown spongy deposit was found on the platinum foil. This was carefully washed with water, dissolved in nitric acid, and the solution evaporated to dryness. On dissolving the residue in hydrochloric acid, and passing hydrogen sulphide gas through the solution, the characteristic reaction for lead was given. No deposit was found on the positive pole. The experiment was repeated, using varying amounts of the lead-nitrate solution, and in every case was a similar deposit found on the negative electrode, which gave the confirmatory reactions for lead. At no time was a deposit found on the platinum dish—the positive electrode.

While these results were satisfactory for the detection of lead in urine to which a lead solution was directly added, results entirely different were obtained with urine in which the lead that was present had been previously assimilated by the system. Fortunately, for this purpose it was not necessary to inject animals with a lead solution, as the urine from several cases of acute lead-poisoning (both before and after treatment with potassium iodide) was placed at the author's disposal by the officers of the University Hospital. In all the samples of urine (some 25 in all) that were examined for lead by the electrolytic method just given, both with and without the presence of nitric acid, in no case was a deposit found on either the positive or negative pole sufficiently large to give a confirmatory reaction for lead on dissolving the deposit in nitric acid, evaporating the solution to dryness with hydrochloric acid, and then adding hydrogen sulphide. In one or two cases the current was allowed to run for five days, and increased to 3 cubic centimetres of oxyhydrogen gas per minute. The oxidising action of the current was so strong that at the end of this time the scum and mucus which separated on the surface of the solution during the earlier passage of the current had entirely disappeared. Even then no deposit was found either on the dish or on the foil that would react for lead. That lead was present in these samples of urine was proved by taking the solutions on which the current had no effect, and rapidly oxidising tbe organic matter present with potassium chlorate and hydrochloric acid. When the solution had become colourless, the excess of hydrochloric acid was evaporated, and hydrogen sulphide gas passed into the solution. The precipitates that were thus obtained were re-dissolved in nitric acid, and further tested for lead with sulphuric acid and potassium chromate. Every sample of urine examined in this manner showed the presence of lead.

These results are of interest, since they show that lead salts passed through the system are, by the time they become components of the urine, of such a composition that they cannot be decomposed by any but the strongest reagents. In the cases cited the lead is probably in combination with the organic acids present in the urine, and in such a stable form that a current of the strength used is not sufficient to break up this combination into its constituents.

For detecting lead in urine, the author has invariably obtained good results by first oxidising the organic matter with potassium chlorate and hydrochloric acid. If desirable, the lead can then be determined electrolytically, as advised by Lehmann. This method, however, is time-consuming. The test for lead with hydrogen sulphide is not alone rapid, but so delicate that preference would be given to it, particularly where the amounts of lead present are small.—*Therapeutic Gazette.*

# ACTION OF THE HALOID ACIDS, IN GAS FORM, UPON MOLYBDIC ACID.*

By EDGAR F. SMITH and VICKERS OBERHOLTZER.

Debray (*Comp. Rend.*, xlvi., 1098, and *Ann. der Chem. und Pharm.*, cviii., 250) first called attention to the fact that a very volatile crystalline compound of the formula $MoO_3.2HCl$ resulted upon exposing molybdic acid, heated from 150—200° C., to the action of hydrochloric acid gas. It is true that the constitution of this volatile product may also be represented by the formula—

$$MoO(OH)_2Cl_2,$$

which would make it a molybdenum hydroxychloride. Dismissing the question of constitution for the present, and considering the point of ready volatility, it seemed to us that this behaviour might be utilised for the separation of molybdic acid from tungstic acid, as the latter apparently does not enter into volatile combination with hydrochloric acid gas. We therefore exposed weighed amounts of sublimed molybdic acid to the action of the acid gas, and succeeded in expelling the molybdic acid completely from the porcelain boats containing it. Applying the same treatment to what we considered pure tungstic acid, we were greatly surprised to discover that very appreciable quantities of a sublimate, similar in every respect to that of molybdenum hydroxychloride, were expelled from the boat. An examination of this product proved it to be the molybdic acid compound. In short, our tungstic acid was not pure. We, however, continued to heat portions of it in hydrochloric acid gas until a sublimate was no longer formed, when, on mixing molybdic acid in known amount with the residual tungstic acid, we discovered that we could completely expel the former acid from the latter. Our next step was to observe the effect of heating anhydrous sodium molybdate in hydrochloric acid gas. The appended results show a quantitative conversion into sodium chloride, consequently a complete volatilisation of the molybdic acid.

| $Na_2MoO_4$ in Grms. | NaCl. | NaCl required. |
|---|---|---|
| 0·1302 gave at 150—200° .. .. | 0·0738 | 0·0739 |
| 0·1832 .. .. | 0·1038 | 0·1040 |
| 0·2046 .. .. | 0·1159 | 0·1162 |
| 0·3845 .. .. | 0·2186 | 0·2183 |

As we were about to apply this method to the quantitative separation of molybdic and tungstic acids, both present as sodium salts, a closer scrutiny of the existing literature relating to this subject revealed that E. Péchard (*Compt. Rend.*, cxiv., 173, and *Zeit. f. Anorg. Chem.*, i., 162) had already carried out the determination of molybdic acid and its separation from tungstic acid in this way with very evident success. Our own experiments confirm those of Péchard in every particular.

As previously observed, the tungstic acid that we thought pure contained molybdic acid. Traube (*Neues Jahrbuch fur Mineralogie, Geologie, und Palæontologie, Beilageband*, vii., 232) has demonstrated that natural calcium tungstate, scheelite, and commercial tungstic acid obtained from the mineral wolframite, contain molybdic acid. E. Corleis (*Liebig's Annalen*, ccxxxii., 265) has shown that the latter acid is even present in the "Wolframsaeure puriss" of trade, while Friedheim (*Zeit. f. Anorg. Chem.*, i., p. 76) asserts that commercial sodium tungstate is strongly contaminated with sodium molybdate, and that, even when exercising the greatest care in the process of purification, the tungstate continued to show traces of molybdenum.

We found molybdic acid present in the purest sodium tungstate that we could get, and in the minerals scheelite and wolframite, when these were exposed to the action of hydrochloric acid gas at a temperature not exceeding 400° C. Hence we are disposed to regard this method as excellently adapted for the detection of molybdic acid, as well as for the purification of tungstic acid and tungstates containing molybdenum.

Our original purpose having been the study of the behaviour of molybdic acid in atmospheres of all the gaseous haloid acids, we may now briefly recount our experiences in those directions.

*Action of Hydrobromic Acid, in Gas Form, upon Molybdic Acid.*—The molybdic acid used by us was purified by converting the commercial acid into the ammonium salt, which was re-crystallised a number of times, and then ignited with air access. The product was sublimed very carefully from a platinum crucible. The hydrobromic acid was prepared by dropping bromine from a separatory funnel upon crude anthracene contained in a half-litre flask. It passed through a hard glass tube, 6 inches in length, filled with anthracene, then through two U-tubes containing a paste of amorphous phosphorus, and two U-tubes provided with fused calcium chloride, while the sixth and last tube contained phosphoric anhydride. Having completed this circuit it was admitted to a perfectly dry combustion-tube, into which had been introduced a porcelain boat filled with molybdic acid. The anterior portion of the combustion-tube was closed with a calcium chloride tube to exclude all moisture. The heat used in the experiment was supplied from a combustion-furnace. An ordinary thermometer was placed above the combustion-tube; its bulb rested directly over the boat. In this manner we recorded the approximate temperature at which the reaction took place. As soon as the entire apparatus was filled with the gas, three burners of the furnace, directly under the boat, were lighted, and the heat gradually raised until it reached 200° C. A change took place almost instantly. Just beyond the boat appeared a heavy sublimate, with a colour resembling that of potassium permanganate. Beyond this solid a brownish-yellow coloured liquid separated; on cooling it changed to long, beautiful yellow needles; these proved to be unstable, melting almost immediately when brought in contact with the air. At the expiration of an hour the passage of the hydrobromic acid gas was interrupted. The permanganate-coloured sublimate was removed from the sides of the tube as completely as possible, introduced into a porcelain boat, and then carefully re-sublimed in a current of dry carbon dioxide. The compound sublimed in fern-like aggregates, consisting of dark red or purple-red, shining, overlapping plates, extending from one side of the combustion-tube to the other. They dissolved in water with liberation of heat. Their aqueous solution was colourless, but upon standing became blue in colour. The crystals themselves changed in appearance on prolonged exposure to the air. By preserving them in an atmosphere of carbon dioxide they suffered no decomposition. Examined under a polarisation microscope they showed their ability to polarise light, and that they consisted of aggregations of perfectly square plates. After the re sublimation portions of the substance were weighed off in weighing tubes, and analysed. For the bromine determination the material was dissolved in as little cold water as possible, dilute nitric acid added, and this followed immediately with silver nitrate. The resulting silver bromide was treated in the usual manner. In estimating the molybdenum, the substance was brought into a weighed porcelain crucible, and dilute nitric acid added. The solution was evaporated almost to dryness at a very gentle heat, when the crucible contents were treated with concentrated nitric acid, after which followed evaporation to perfect dryness. This operation was repeated, and a gentle but direct heat applied to the crucible for periods varying from one-half to one hour. This was done to fully oxidise the molybdenum to trioxide. Portions of the new compound were mixed with freshly-ignited litharge, and heated in a current of dry air, using a perfectly dry combustion-tube, provided with a weighed

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* Read before the Chemical Section of the Franklin Institute, April 18th, 1893.

calcium chloride tube. The weight of the latter showed no increase, so that we were safe in considering our substance free from hydrogen.

### ANALYSES.

#### *Bromine Determination.*

| | AgBr. Grms. | | Bromine Percentage. |
|---|---|---|---|
| 0·1334 grms. substance gave.. | 0·1793 | = | 57·19 |
| 0·3353 .. | 0·4499 | = | 57·09 |
| 0·0680 .. | 0·0908 | = | 56·82 |

The mean of these bromine percentages is 57·037 per cent.

#### *Molybdenum Determination.*

| | $MoO_3$. Grms. | | Molybdenum Percentage. |
|---|---|---|---|
| 0·2545 grms. substance gave.. | 0·12865 | = | 33·69 |
| 0·2916 .. | 0·1466 | = | 33·52 |
| 0·1115 .. | 0·0559 | = | 33·42 |

The mean of the molybdenum percentages is 33·54 per cent.

We experienced difficulty in wholly eliminating the traces of blue oxide in all of the molybdenum determinations; hence we look upon the results given above as low.

Regarding our compound as consisting of molybdenum, bromine, and oxygen, with the above percentages, and taking the oxygen by difference, we deduce, as the most probable formula, $MoO_2Br_2$, $MoOBr_2$, or $Mo_2O_3Br_4$,—molybdenum sesquioxide tetrabromide. The theoretical requirements of this formula are:—34·28 per cent Mo, 57·19 per cent Br, and 8·57 per cent O.

The only existing molybdenum oxybromide until the present has been $MoO_2Br_2$,—molybdenyl bromide, discovered by Blomstrand on passing bromine vapour over the heated dioxide of molybdenum, or by heating a mixture of molybdic acid and boron trioxide with potassium bromide. It is mentioned as forming yellow deliquescent tablets. For the sake of comparison, we made Blomstrand's compound by the second method. We found that when it was sublimed upon a previously heated portion of the tube it separated in "mehr ausgebildeten Krystalltafeln auf; bei rascher Sublimirung in undeutlich krystallinischen Schuppen. Farbe schön gelbroth." (Blomstrand, *Jour. Prakt. Chem.*, lxxxii., 439). Our compound, however, is formed simultaneously with that of Blomstrand when vapours of bromine are conducted over heated molybic acid; the tube in which this reaction was made was freed from air by conducting bromine vapours through it, and heat was not applied until we were satisfied that bromine alone was present.

The brownish-yellow liquid formed at the same time with the purple-red coloured solid was crystallised in the tube in which it had been produced; the tube was then severed at a point between the yellow and red-coloured compounds. The yellow immediately liquefied on exposure to the air. The liquid was collected in a small and previously weighed beaker; this was then placed in a sulphuric acid desiccator and the air exhausted. At the expiration of from two to three days the yellow needles had re-formed. The beaker and its contents were then rapidly weighed. Water was poured on the needles; their sloution was colourless or slightly yellow tinged. On standing, the liquid slowly acquired a deeper yellow or reddish yellow hue, and after twenty-four hours a blue oxide of molybdenum had separated.

The bromine and molybdenum of this product were determined in the same manner as in the purple-coloured solid. We, however, had no difficulty in obtaining perfectly white molybdic acid in all the determinations that follow:—(See Table, next column).

### ANALYSES.

#### *Bromine Determination.*

| | Silver Bromide. Grms. | | Bromine Percentage. |
|---|---|---|---|
| 0·0250 grms. substance gave.. | 0·1403 | = | 62·83 |
| 0·2523 .. | 0·3700 | = | 62·50 |
| 0·2709 .. | 0·3967 | = | 62·37 |
| 0·0250 .. | 0·0365 | = | 62·12 |

The mean percentage equals 62·45 per cent.

#### *Molybdenum Determination.*

| | $MoO_3$. Grms. | | Percentage of Mo. |
|---|---|---|---|
| 0·0946 grms. substance gave.. | 0·0346 | = | 24·39 |
| 0·0946 .. | 0·0337 | = | 23·75 |
| 0·1892 .. | 0·0686 | = | 24·06 |

The mean of these percentages is 24·03 per cent. The formula we deduce from these results is $MoO_3{\cdot}3HBr$; it perhaps might be better represented as a trihydroxybromide, $MoO(OH)_3Br_3$. The theoretical requirements are 62·02 per cent Br, and 24·80 per cent Mo.

It is interesting to note that the long yellow-coloured needles of this compound were also obtained upon passing hydrobromic acid gas over the oxybromide of Blomstrand at a gentle heat. This change may easily be conceived as occurring if we grant the presence or production of water through the formation of secondary products.

$$MoO_2Br_2+H_2O+HBr=MoO_3{\cdot}3HBr.$$

As we were not in a position to ascertain the true composition of the individual substance or substances from scarcity of material, we offer the above suggestion as a possible explanation for the appearance of the hydroxybromide in the manner just indicated.

*Action of Hydriodic Acid, in Gas Form, upon Molybdic Acid.*—A violent reaction occurred, in the cold upon passing the dry acid gas over molybdic acid; much heat was evolved, and iodine was liberated. The non-volatile product that remained in the boat possessed a bright violet colour. It was exposed for a period of two hours to a temperature ranging from 45° to 50° C., during which time a continuous stream of dry and pure gas was conducted over it. Carbon dioxide was next introduced and passed for an equal period, while the temperature was maintained at 50° C. The results obtained from many analyses of this product pointed to the probable composition $MoO_3HI$; but as the quantity of iodine varied according to the length of time during which the hydriodic acid gas acted and with the temperature, we feel unable to assign any definite composition to the compound. It has seemed to us, from a careful study of the experimental results, that several derivatives were formed, but we were unable to separate them; and indeed, by continuing the action of the gas for periods varying from six to eight hours, at the same time elevating the temperature from 105° to 120° C., iodine continued to separate. At last a violet-blue coloured product remained; this appeared to be homogeneous. Prolonged action of the gas was without further reduction, therefore carbon dioxide was introduced to expel it. The blue-coloured product suffered no change on exposure to the air. We obtained what appeared to be the same substance by exposing the iodine-containing compound mentioned above to a temperature of 200° C., in an atmosphere of carbon dioxide. Indeed, mere exposure of the iodine compound to the air for some time gave the blue-coloured derivative.

The same form of apparatus was used here that we have described with the oxybromides. The hydriodic acid gas was made from moist phosphorus and iodine. It was carefully dried.

*Analyses.*—An analysis of the blue-coloured residue resulted as follows: the molybdenum was determined as under the bromine derivatives:—

| | $Mo_3O$. Grms. | | Mo Per cent. |
|---|---|---|---|
| 0·1099 grms. substance gave.. | 0·1053 | = | 64·19 |
| 0·1017 .. | 0·0972 | = | 63·72 |
| 0·0807 .. | 0·0775 | = | 64·02 |
| 0·0959 .. | 0·0937 | = | 64·92 |
| 0·1386 .. | 0·1350 | = | 64·93 |

The mean molybdenum peccentage is therefore 64·35 per cent.

*Water Determination.*

| | $H_2O$. Grms. | | Per cent. |
|---|---|---|---|
| 0·1533 grms. substance gave.. | 0·0138 | = | 9·00 |
| 0·1673 .. | 0·0142 | = | 8·49 |

The mean of these percentages would therefore be 8·74 per cent. An intense red heat was required to fully expel this water content. The figures obtained would lead to an oxide of the formula $Mo_4O_{10},3H_2O$; this would require 64·21 per cent Mo and 9·03 per cent $H_2O$. Iodine was not found in the compound. The dehydrated residue was brown in colour. Three determinations of its molybdenum content indicated it to be $Mo_2O_5$. As a result, then, of the action of hydriodic acid gas upon molybdic acid, we can point to no definitely iodated product, but to a blue oxide, a product of reduction. In this connection we may direct attention to the observation of Schulze (*Journ. Prak. Chem.* (N. F.), xxix., 440), that molybdic acid sustains reduction when heated with potassium iodide, air being excluded. The resulting products possess variable composition, but by the use of four parts of molybdic acid and one part of potassium iodide a definite product was prepared. It proved to be a new oxide of molybdenum, steel-blue in colour, crystalline, and possessing metallic lustre. Its analysis gave results agreeing with the formula $Mo_4O_{11}$. Our reduction product is quite analogous to this, except that it is hydrous.

*Action of Hydrofluoric Acid, in Gas Form, upon Molybdic Acid.*—The hydrofluoric acid gas was evolved from fluorspar and sulphuric acid. It passed directly over the molybdic acid contained in a platinum boat, and the latter in a platinum combustion-tube from which a delivery-tube led into a platinum flask, cooled by ice-water. At a temperature ranging from 300° to 400° C., all the molybdic acid was converted into a volatile product that collected upon the anterior portions of the platinum combustion-tube in crystals, having a peculiar red colour. On holding the tube in which these crystals had been sublimed toward the light, it appeared to be filled with violet vapours of iodine; this was, however, due to reflection of light from the sides of the flat needle-like crystals. It is scarcely necessary to remark that before disconnecting the apparatus, carbon dioxide was conducted through it to expel the hydrofluoric acid. The platinum flask also contained the volatile molybdenum product. Much hydrofluoric acid was with it. This was expelled by the introduction of the carbon dioxide.

The new product when removed from the vessels containing it was found to be deliquescent, and it gradually decomposed into a blue oxide of molybdenum. It attacked glass, was insoluble or nearly insoluble in water, but dissolved to a colourless liquid in hydrofluoric acid. Portions of it were weighed off as rapidly as possible in platinum crucibles, and the molybdenum determined as trioxide by evaporation with nitric acid, followed by gentle ignition.

*Molybdenum Determination.*

| | $MoO_3$. Grms. | | Mo. Per cent. |
|---|---|---|---|
| 0·0526 grms. substance gave.. | 0·0479 | = | 60·70 |
| 0·1066 .. | 0·0967 | = | 60·66 |
| 0·1166 .. | 0·1c51 | = | 60·94 |
| 0·1265 .. | 0·1164 | = | 61·35 |

The mean of these determinations is 69·91 per cent Mo. Formed in the same manner as molybdenum sesquioxide tetrabromide, we find that these results agree very closely with an oxyfluoride of analogous formula, $Mo_2O_3Fl_4$, which would require 60·76 per cent Mo. In experimenting with the above oxyfluoride we several times observed a slight quantity of a colourless liquid, which upon careful evaporation with nitric acid left a very apreciable quantity of molybdic acid. It may, perhaps, be an analogue of the very volatile $MoO_3{\cdot}2HCl$, and the unstable liquld $MoO_3.3HBr$. We endeavoured to fix its composition, but experienced so great difficulty in getting material that we could safely consider sufficiently pure that we abandoned it entirely. The work attending its preparation is anything but pleasant, and the yield exceedingly uncertain.

But one other oxyfluoride of molybdenum is known; namely, that prepared by Schulze (*Journ. Prakt. Chem.* (N. F.), xxi., 442), by fusing metallic fluorides together with molybdic acid with the exclusion of air. It has the constitution represented by the formula $MoO_9Fl_2$.

Reviewing the action of the gaseous haloid acids upon molybdic acid we observe:—

(1.) That hydrochloric acid gas converts the acid into a solid, very volatile product, $MoO_3{\cdot}2HCl$.

(2.) That hydrobromic acid changes molybdic acid to a volatile brownish-yellow liquid, $MoO_3.3HBr$, forming long yellow needles at low temperatures and under diminished pressure, as well as a beautifully crystallised solid of the formula $Mo_2O_3Br_4$.

(3.) That hydriodic acid reduces molybdic acid to a new oxide, $Mo_4O_{10}.3H_2O$.

(4.) That hydrofluoric acid converts the molybdic acid into at least one well-formed but volatile product, having the constitution represented by the formula $Mo_2O_3Fl_4$.

Püttbach (*Annalen*, cci., 137) divides the known molybdenum oxychlorides into two classes:—

| Saturated. | Unsaturated. |
|---|---|
| $MoOCl_4$ | $Mo_3O_3Cl_7$ |
| $Mo_2O_3Cl_6$ | . |
| $Mo_3O_5Cl_8$ | $Mo_2O_3Cl_4$ |
| $MoO_2Cl_2$ | |

But one oxybromide is known. Its formula is $MoO_2Br_2$. Our experiments add to this the compound $Mo_2O_3B_4$, which would correspond to $Mo_2O_3Cl_4$. The latter is light brown in colour, while the former possesses a deep purple colour. Schulze's oxyfluoride would correspond to $MoO_2Cl_2$ and $Mo.O_2Br_2$, while that obtained by us corresponds to $Mo_2O_3Cl_4$ and $Mo_2O_3Br_4$. Püttbach's division presupposes the presence of a sexivalent molybdenum atom in the saturated members, while the unsaturated are regarded as derived from two molecules of $MoCl_5$ by the substitution of oxygen for equivalent amounts of chlorine. Our oxybromide, $Mo_2O_3Br_4$, and oxyfluoride, $Mo_2O_3Fl_4$, may be looked upon as possessing similar origin, although their corresponding pentabromide and pentafluoride are unknown. The compound $MoO_3.3HBr$, like $MoO_32HCl$, presupposes the presence of a sexivalent molybdenum atom, and may be properly considered a hydroxybromide, represented by the formula $Mo(OH)_3Br_3$, a derivative of the unknown hexabromide $MoBr_6$.

## REACTION FOR CERIUM OXIDE.

By H. C. PLUGGE.

The author recommends a solution of strychnine in concentrated sulphuric acid as a characteristic and sensitive reagent.

If to a trace of cerium hydroxide precipitated by alkalies, almost dried on the filter, and then placed in a porcelain capsule, we add a few drops of the above-mentioned solution of strychnine, there appears at once a splendid blue colour, which soon disappears, and is succeeded by a more permanent cherry-red or faint red according to the quantity of the cerium oxide contained in the precipitate. This reaction is an inversion of Sonnenschein's well-known reaction for strychnine. Plügge used a solution of 1 part of strychnine (or its nitrate or sulphate) in 1000 parts of concentrated sulphuric acid, as also a solution of cerium oxide in a slight excess of dilute sulphuric acid, the latter diluted with so much water that 1 c.c. of the solution contains 1 m.grm. cerium oxide.

Of this solution of cerium quantities accurately measured were each time evaporated down, and two, three, or more drops of the reagent were added to the dry residue when cold. The residues from 10 and from 5 c.c. solution of cerium sulphate were strongly coloured, but those from 1 and even from 2½ c.c. of this liquid showed no perceptible colouration. With the salts of cerium (sulphate, oxalate, &c.) the reaction is not remarkably sensitive. But with the following modification it becomes so delicate that the limit of sensitiveness can be taken as 0·00001 grm. cerium oxide. A little of the solution of the cerium salt with the addition of so much dilute soda-lye as may serve to render the liquid distinctly alkaline is evaporated in a capsule, and the dry residue is covered with a few drops of the strychnine solution. For very dilute solutions containing little free acid a single drop of very dilute soda-lye is sufficient, so that the excess of alkali in the evaporated residue will neutralise but very little of the sulphuric acid of the reagent.

With this modification the evaporated residue of 1 c.c. solution containing 1 part of cerium oxide in 100,000 c.c. (*i.e.*, 0·01 m.grm. cerium) gave a distinct violet colour, which, however, soon disappeared. The residue from the evaporation of 10 c.c. of this solution (0·1 m.grm.) gave under the same conditions a very strong reaction, at first blue and then a permanent red.

Whilst very small quantities of cerium oxalate do not become coloured if covered with the above reagent, similar quantities of this salt, after previous heating or moistening with a little dilute soda-lye, and drying on the water-bath, are very strongly coloured.

The precipitate thrown down by alkalies from solutions of the cerium salts may, after desiccation, be used at once for Plugge's reaction. If this reagent is applied to the white precipitate produced by ammonium chloride and ammonia in a mixed solution of zinc, aluminium, and cerium it easily shows the presence of cerium along with aluminium. This does not, however, directly succeed in the white precipitate given by ammonium chloride, ammonia, and ammonium sulphide, as then, on adding the above reagent, $H_2S$ is liberated from the zinc sulphide, which destroys the colour or prevents its formation.—*Archiv der Pharmacie* and *Zeitschrift fur Analytische Chemie.*

## ON AMIDOPHOSPHORIC ACID.*

By H. N. STOKES.

By replacing the hydroxyls of orthophosphoric acid successively by amido groups, three amides may be derived, namely, amidophosphoric acid, $PO.NH_2.(OH)_2$, diamidophosphoric acid, $PO.(NH_2)_2.OH$, and phosphoryl triamide, $PO(NH_2)_3$, and from these, by abstraction of water or ammonia, an imido acid, $PO.NH\ OH$, an imidoamide, $PO.NH.NH_2$, and a nitrile, $PO.N$. Of these, amido- and diamidophosphoric acids have not yet been described. In the dictionaries of Fehling (*Neues Handworterbuch der Chemie*, v., 423), and of Ladenburg (*Handworterbuch der Chemie*, ix., 100) the formula $PO.NH_2.(OH)_2$ is given to a body described by Schiff (*Ann. Chem.* (*Liebig*), ciii., 168), and called by him *phosphaminsaeure*. This rests on an error of the compilers, as Schiff gives to his acid the formula $PO.NH.OH$, with which his analyses agree, while they differ widely from that of amidophosphoric acid. Moreover, as will be shown, amidophosphoric acid is a body of entirely different properties.

Schiff (*Ann. Chem.* (*Liebig*), ci., 300) also describes the triamide, $PO(NH_2)_3$. Although his analyses agree quite well with this formula, the existence of the body is called in question by Gladstone (*Jour. Chem. Soc.*, [2], vii., 18), who, in repeating Schiff's method of preparation, treating phosphorus oxychloride with dry ammonia, was unable to replace the third chlorine atom at any temperature below that at which further decomposition occurs (above 300°). The correctness of the formula $PO.NH.OH$ assigned by Schiff to his phosphamic acid is also questioned by Gladstone and Holmes (*Jour. Chem. Soc.*, [2], ii., 229, 235), who point out the general resemblance of its properties, as described, to those of pyrophosphodiamic acid obtained by them. They regard it as a mixture of the latter with metaphosphoric acid. The identity of Schiff's acid with pyrophosphodiamic acid (diamidopyrophosphoric acid) has also found acceptance in some handbooks (Gmelin-Kraut, *Handbuch der Anorg. Chemie*, i., 2 Abth., 529; Graham-Otto, *Anorg. Chem.* (*Michaelis*), ii., 401).

The imidoamide, $PO.(NH).NH_2$, was described by Gerhardt (*Ann. Chim. Phys.*, [3], xviii., 188) under the name phosphamide, and was obtained by treating phosphorus pentachloride with dry ammonia and then with water. Its nature has not been questioned.

The body $PO.N$, described by Gerhardt (*Ann. Chim. Phys.*, [3], xviii., 188) as biphosphamide, by Schiff (*Ann. Chem.* (*Liebig*), ci., 304) as monophosphamide, and by Gladstone (*Jour. Chem. Soc.*, [2], vii., 18) as phosphonitryle, is the final product of heating the triamide, the imidoamide or the amido chlorides. Its constitution is not known, but is probably much more complex than is represented by the formula given.

In addition to the above, Gladstone and Holmes (*Quar. Journ. Chem. Soc.*, iii., 353; *Journ. Chem. Soc.*, [2], ii., 225; [2], iv., 1290; [2], vi., 64, 261; [2], vii., 15) have obtained a series of complex amides, derivable from pyro- and tetraphosphoric acids.

The difficulty in preparing amido orthophosphoric acids lies in part in the impossibility of regulating the decomposition by water or acids of the products of the action of ammonia on phosphorus pentachloride and oxychloride. Gerhardt's imidoamide and Schiff's triamide seem to be capable of giving ammonia and phosphoric acid only; at least no mention is made of intermediate products. The bodies derived from phosphorus oxychloride by partial replacement of chlorine by amido groups are so decomposed by water as to give the amidopyrophosphoric acids of Gladstone, and further action results in the separation of ammonia before the pyrophosphoryl group is broken up. The reason for this, as will be seen below, lies in the great ease with which amidophosphoric acid passes over into ammonium phosphate. As phosphorus pentoxide is a derivative of pyrophosphoric acid, it is not to be expected that it would give orthophosphoric amides with ammonia.

I have overcome these difficulties in part, by acting with ammonia on phosphoric ethers, and in this way have obtained the primary amide, $PO.NH_2.(OH)_2$. Attempts to obtain other amides by the same method are in progress.

By dissolving the chloride of diphenylphosphoric acid, $PO.Cl.(OC_6H_5)_2$, in alcohol, and adding alcoholic ammonia, diphenylamidophosphate, $PO.NH_2.(OC_6H_5)_2$, a beautifully crystalline substance is at once formed. This, on saponifying with ammonia or baryta, gives phenylamidophosphoric acid, $PO.NH_2.(OC_6H_5).(OH)$, and with caustic potash or soda amidophosphoric acid. The free acid obtained by decomposing the lead salt by sulphuretted hydrogen and precipitating with alcohol is a well characterised body, forming fine microscopic crystals. It forms two series of salts, acid and neutral, of which the acid salts are invariably, the neutral often, crystalline, and in many cases the forms are characteristic. Boiled in aqueous solution, either alone or with an acid,

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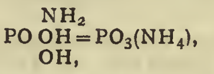
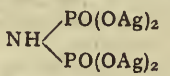
* *American Chemical Journal*, vol. xv, No. 3.

it decomposes amost instantly into ammonia and orthophosphoric acid. Its cold aqueous solution may be kept a short time without much decomposition, but quickly passes into primary ammonium orthophosphate. Dilute mineral acids in the cold effect the change much more rapidly, but in either case the first product is not orthophosphoric acid, but an acid or mixture of acids giving white amorphous precipitates with silver nitrate. At 100° the dry acid passes without loss of weight into an ammonium salt, giving a white silver salt. This is possibly metaphosphate, or a mixture of the different metaphosphates,—



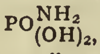
$$PO\begin{smallmatrix}NH_2\\OH\\OH,\end{smallmatrix}=PO_3(NH_4),$$

but the nature of the product has not yet been established. The acid salts on heating give off ammonia and leave metaphosphates. Such of the neutral salts as contain crystal water pass first into ammonium salts, and on further heating into pyrophosphates. The neutral silver salt, which is anhydrous, is an exception. At 180° it gives off one-half its nitrogen as ammonia, apparently forming a very stable *pyrimidophosphate*,



$$NH\begin{smallmatrix}PO(OAg)_2\\PO(OAg)_2\end{smallmatrix}$$

which stands a red heat without further change, or at least without loss of weight. Other salts which are especially characteristic are the acid sodium salt, almost insoluble in water, and the neutral magnesium salt, isomeric with crystallised ammonium magnesium phosphate. In the absence of any experimental proof of the contrary, the constitution of the acid is regarded as—



$$PO\begin{smallmatrix}NH_2\\(OH)_2,\end{smallmatrix}$$

in accordance with the usually assumed structure of acid amides, rather than as $P(NH)(OH)_3$, in harmony with the most recent views on the nature of organic amides.

### DESCRIPTIVE PART.

*Diphenylamidophosphate.* $PO\begin{smallmatrix}NH_2\\(OC_6H_5)_2.\end{smallmatrix}$—One mol. wt. phosphorus oxychloride and 2 mol. wts. phenol are boiled in a flask fitted with return condenser until no further evolution of hydrochloric acid occurs. The product is a mixture of—

$$PO(OC_6H_5)_3,PO.Cl.(OC_6H_5)_2,PO.Cl_2.(OC_6H_5)$$

and unchanged oxychloride. It is not necessary to isolate the diphenylphosphoric chloride. The liquid is diluted with absolute alcohol, and alcoholic ammonia is added slowly, with cooling, to alkaline reaction. The product is mixed with several volumes of water, whereby ammonium chloride dissolves and crystalline amidophosphate separates, mixed with oily phenylphosphates. This is sucked out in a funnel as far as possible, washed with water, dried on porous plates to remove the oil, again washed, dried, and re-crystallised two or three times from alcohol, or better, chloroform. The yield is about 35 per cent of the theoretical.

| | Calculated or $PO.NH_2.(OC_6H_5)_2$. | | Found. | |
|---|---|---|---|---|
| P | 12·46 | — | 12·37 | — |
| N | 5·67 | 5·70 | 5·64 | 5·67 |

Phosphorus was determined as magnesium pyrophosphate after evaporating first with alkali, then with acid; nitrogen as ammonia after evaporating with hydrochloric acid; both as ammonium chloroplatinate and by titration, after distilling.

The ether fuses at 148°, and on cooling solidifies to a crystalline mass with a surface of brilliant facets. At 180° there is a very slow evolution of ammonia and phenol, which becomes quite rapid at 230°, when it is accompanied by sublimation of unchanged substance. The non-volatile product of decomposition is first an oil, later a solid substance containing phosphorus.

*Phenylamidophosphoric acid*, $PO\begin{smallmatrix}NH_2\\OC_6H_5.\\OH\end{smallmatrix}$ — The free acid could not be obtained in the solid state. On decomposing the lead salt in the cold with sulphuretted hydrogen a solution is obtained which is not precipitated by alcohol. On evaporating *in vacuo* over sulphuric acid, the acid takes up water, and is converted into the acid ammonium salt of phenylphosphoric acid, which contains only traces of amido acid, which were isolated as the silver salt described below.

*Acid ammonium phenylphosphate* is easily soluble in water, and crystallises in long prisms. It also crystallises from alcohol, in which it is difficultly soluble, as pearly rhombic plates or flat needles, fusing at 140—145° with decomposition. Silver nitrate gives a precipitate of radiating flat prisms consisting of the *neutral silver salt* (*a*) which is anhydrous. By neutralising the filtrate with ammonia a further precipitate of the same salt (*b*) is obtained.

| | Calculated for $PO\begin{smallmatrix}(OAg)_2\\OC_6H_6\end{smallmatrix}$ | Found.<br>(*a*) | <br>(*b*) |
|---|---|---|---|
| Ag | 55·64 | 54·88 | 55·44 |

Phenylphosphoric acid therefore resembles phosphoric acid in that its acid salts give directly the neutral silver salt, and differs from amidophosphoric acid, which gives either acid or neutral silver salt according as acid or neutral salt be used as precipitant.

*Ammonium phenylamidophosphate*, $PO\begin{smallmatrix}NH_2\\OC_6H_5,\\ONH_4\end{smallmatrix}$ obtained by saponifying the diphenyl ether with aqueous ammonia, is easily soluble in water, and the solution may be evaporated without decomposition.

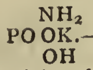
*Silver phenylamidophosphate*, $PO\begin{smallmatrix}NH_2\\OC_6H_5,\\OAg\end{smallmatrix}$ from the ammonium salt, after recrystallising from water, forms scales, or long. narrow, pointed plates of pearly lustre. It is difficultly soluble in cold, moderately in boiling water, and has a strong tendency to separate as a crystalline scum on the surface. It is unaffected by light.

| | Calculated for $PO(NH_2)(OC_6H_5(OAg)$. | | Found. | |
|---|---|---|---|---|
| P | 11·09 | — | 11·11 | — |
| N | 5·02 | — | 5·08 | — |
| Ag | 38·53 | 38·31 | — | 38·19 |

*Barium phenylamidophosphate* is formed by boiling the ether with baryta water until nothing crystallises out on cooling, and removing the excess of baryta by carbon dioxide. It forms scales, is quite soluble in water, and resembles the silver salt in forming a crystalline scum on the surface.

*Lead phenylamidophosphate*, from the barium salt by lead acetate, forms brilliant scales, nearly insoluble in water.

*Amidophosphoric acid*, $PO\begin{smallmatrix}NH_2\\(OH)_2.\end{smallmatrix}$ — The alkali salts of this acid are readily obtained by saponifying the ether with a strong solution of caustic potash or soda. The chief difficulty in obtaining them pure is in separating them from the small quantity of phosphate formed at the same time. In the case of some of the salts this may be effected by methods mentioned below. The conversion into phosphate by boiling alkali is very slow. A weighed amount of ether was boiled with concentrated caustic potash, and the ammonia determined in the distillate by titration. An hour's boiling showed a decomposition of only 3 per cent.

*Acid potassium amidophosphate*,  $PO\begin{matrix}NH_2\\OK\\OH\end{matrix}$.—If a lump of caustic potash be placed on some diphenyl ether, and a few drops of water be added, a somewhat violent reaction occurs. On boiling with an excess of concentrated caustic potash, the saponification is complete in ten minutes. The oily solution is acidified with strong acetic acid, care being taken to keep it cool with ice-water. On adding several volumes of alcohol, the acid salt is at once precipitated. It is purified by washing with alcohol, dissolving in a little water, and re-precipitating by alcohol. It cannot be re-crystallised from hot water, as its solution is rapidly converted by heating into acid potassium ammonium phosphate. A weighed amount of acid potassium salt was dissolved in water and boiled ten minutes; $\frac{1}{10}$ *n*. caustic soda was added in excess, and the solution again boiled to remove ammonia. The loss of alkalinity due to the escape of ammonia indicated that, by ten minutes' boiling, 98 per cent of the amide was converted into ammonium salt. The same change occurs in a few days in the cold aqueous solution. The salt forms six-pointed stars, or sometimes rhombohedra, readily soluble in cold water, insoluble in alcohol. Its solution is neutral towards litmus, methyl orange, and phenolphthalein. On ignition it gives off ammonia, and leaves potassium metaphosphate.

The analysis of two air-dried preparations (*a* and *b*) gave—

| | Calculated for $PO.NH_2.OK.OH$. | Found. *a*. | | *b*. |
|---|---|---|---|---|
| P | 22·96 | 22·76 | | — |
| N | 10·39 | 10·26 | 10·20 | 10·35 |

The loss on ignition gave—

| | Calculated for $PO.NH_2.OK.OH$. | Found. |
|---|---|---|
| $NH_3$ | 12·61 | 13·83 |

The excess found is due in part to a small amount of water which the salt retains, in part to a little acid potassium ammonium phosphate which cannot be removed by precipitating with alcohol. The amount of ammonium salt may be determined by distilling off the ammonia with alkali solution, and determining it in the distillate, making a slight correction for the decomposition of the amide itself as above determined (3 per cent per hour). In this way the amount of ammonium salt in preparation (*a*) was found to be 4·75 and 5·10 per cent, in (*b*) 4·15 per cent. As the acid potassium salt is used for preparing other salts, this small amount of phosphate has to be taken into consideration, as the latter would otherwise be contaminated with phosphate. Its presence may be obviated by methods below mentioned.

*Neutral potassium amidophosphate* is extremely soluble in water, and not appreciably decomposed by boiling.

(To be continued).

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**Valuation of Ipecacuanha.**—G. Kottmayer (*Pharm. Post*) mixes 15 grms. of powdered ipecacuanha with 148 c.c. of alcohol at 90 per cent, and 2 c.c. hydrochloric acid of sp. gr. 1·12, and digests for four days at 40° in a stoppered flask, with frequent shaking. 100 c.c. of the perfectly clear liquid, cooled down to 15°, are drawn off with a pipette and mixed in a capsule with 20 c.c. of an alcoholic solution of lead acetate (1 part sugar of lead, 9 parts of alcohol at 50 per cent); 1·5 grms. hydrate of lime are added, and the whole is evaporated down on the water-bath to the consistence of a paste. To this paste he adds 5 grms. of moderately fine glass evaporated to dryness with constant stirring, and the readily friable residue is extracted with chloroform for ten hours. The chloroform solution is evaporated, the dried residue weighed, treated with 2 c.c. normal hydrochloric acid, and the undissolved matter (after careful washing and drying) is weighed again. The difference between the two weights shows the emetine present.

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*Ordinary Meeting, June 23rd, 1893.*

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Prof. J. Cox, M.A., was elected a Member of the Society.

Mr. F. H. Nalder exhibited a Bridge and Commutator for comparing Resistances by Prof. Carey Foster's Method, the chief features of which are simplicity, compactness, long range, and great accuracy. The commutation of the coils to be compared is effected by mercury cups, the eight holes necessary for this purpose being arranged in a circle. An ebonite disc carrying the four connectors is mounted on a spindle in the middle of the circle, and the positions of the coils are interchanged by rotating the disk through 180°. A large range is secured by providing a number of interchangeable bridge wires, and a fine adjustment for the galvanometer key enables great accuracy to be attained.

Mr. W. R. Pidgeon and Mr. J. Wimshurst each read a paper on "*An Influence Machine*," and exhibited their machines in action. In designing his machine Mr. Pidgeon has endeavoured, 1st, to make the capacity of each sector large when being charged and small when being discharged; 2nd, to prevent leakage from sector to sector as they enter or leave the different fields of induction; and 3rd, to increase the capacity of the machine by making the sectors large and numerous. The first object is attained by arranging fixed inductors of opposite sign to the sectors near the charging-points, and of the same sign near the places of discharge. Objects 2 and 3 are secured by imbedding the sectors in wax, run in channels in the ebonite discs which form the plates of the machine, and carrying wires from each sector through the ebonite, each wire terminating in a knob. In this way the sectors can be placed much nearer together than otherwise, without sparking back. By setting the sectors skew with the radius, they are caused to enter the electric fields more gradually,—consequently the potential difference between adjacent sectors is kept comparatively small. Experiment showed that the use of the stationary inductors at the charging-points increased the output threefold, and as compared with an ordinary Wimshurst the output for a given area of plate passing the conductors was as 5·6 : 1. The recovery of the machine after a spark had occurred was particularly rapid.

Mr. Wimshurst's new machine consists of two glass discs, 3 feet 5 inches diameter, mounted about $\frac{3}{4}$" apart on the same spindle. Both plates turn in the same direction. Between the discs are fixed four vertical glass slips, over 4 feet long, two on each side, and each covering about $\frac{3}{8}$ths of a disc. Each slip carries a tin-foil inductor, which has a brush, touching lightly on the inside of the adjacent disc, on its leading edge. Collecting and neutralising brushes touch the outsides of the discs and the few metallic sectors attached thereto. An account of some experiments made to determine the efficiency of the machine was given. The author also showed that when all the circuits of the machine were broken, it still continued to excite itself freely, and sparked from the discs to the hands when brought near.

In a written communication Prof. O. Lodge said his assistant, Mr. E. E. Robinson, constructed a machine on lines similar to Mr. Pidgeon's, a few months ago, and had now a large one nearly completed. Mr. Robinson's fixed inductors are carried on a third plate fixed between the two movable ones. The sectors are quite small, and neither they nor the inductors are embedded. On close circuit the machine gives a large current ($\frac{1}{1000}$ ampère) and on open circuit exceedingly high potentials. In Dr. Lodge's opinion Mr. Pidgeon attaches too much importance to his sectors and their shape.

Mr. J. Gray wrote to say that stationary inductors enclosed in insulating material would probably give trouble at high voltages, because of the surface of the insulator becoming charged with electricity of opposite sign to that on the inductor. He suggested that this might explain why Mr. Pidgeon could not obtain very long sparks.

Prof. C. V. Boys enquired as to how far the wax made insulating union with the ebonite, for, if good, glass might possibly be used instead of ebonite. He greatly appreciated the design of Mr. Pidgeon's machine.

After some remarks by the President, on the great advances which had been made, Mr. Pidgeon replied, and Mr. Wimshurst tried some further experiments with a small experimental machine.

A paper on "*A New Volumenometer*," by Mr. J. E. Myers, B.Sc., describing the developed form of Prof. Stroud's instrument, was, in the absence of the author, taken as read.

Mr. R. W. Paul exhibited a compact form of sulphuric acid voltameter of small resistance. The voltameter is a modification of a pattern designed at the Central Institution, in which the rate of decomposition is determined from the time required to fill a bulb made in the stem of a thistle-funnel. He also showed a handy form of Daniell cell, devised by Prof. Barrett. When not in use, the porous pot containing the zinc is removed from the copper sulphate solution, and placed in a vessel containing zinc sulphate or sulphuric acid.

A paper on "*Long-Distance Telephony*," by Prof. J. Perry, F.R.S., assisted by H. A. Beeston, was read by Prof. Perry. The case of a line of infinite length, having resistance capacity, self-induction, and leakage, is taken up, and the state of a signal as it gets further and further away from the origin is considered. Taking the shrillest and gravest notes of the human voice to have frequencies of about 950 and 95 respectively, the distance from the origin at which the ratio of the amplitudes of these high and low frequency currents is lessened by $1/m$th of itself, has been determined when $m=4$ for different values of leakage and self-induction; and under similar conditions the distances at which the relative phase of the two currents become altered by $1/n$th of the periodic time of the most rapid one, have been worked out for $n=6$. The results are given in the form of Tables, from which it appears that, if there was no self-induction, increasing the leakage increases the distance to which we can telephone, whilst if there was no leakage increasing the self-induction increases the distance. When self-induction and leakage are not so great, increasing either increases the distance, and for particular values the distances become very large. At the end of the paper Tables of general application are given, from which the limiting distances for any line can be readily found by multiplying the numbers by simple functions of the constants of the line.

Mr. Blakesley said that some ten years ago he discussed the subject when capacity and resistance were alone considered, and now pointed out that when self-induction and leakage were introduced, the equations were still of the same form. He also suggested how terminal conditions on lines of finite length might be easily taken into consideration.

Prof. Perry, in reply, said the introduction of self-induction and leakage rendered the calculations much more laborious, and that the terminal conditions were much more complicated than Mr. Blakesley supposed.

## NOTICES OF BOOKS.

*Rules for the Estimation of Alcohol in Imported Spirits.* With Tables giving the Specific Gravity of Alcohol from 984 to 936, computed to the third place of decimals. By C. J. H. Warden, M.D., Medical Examiner to the Government of Bengal. Issued by order of the Board of Revenue, Bengal. Calcutta: Bengal Secretariat Press, 1892.

The manipulation of highly volatile liquids such as commercial spirits in localities where the temperature is high presents considerable difficulties. In the author's laboratory the usual temperature during a great part of the year ranges from 80° to 95° F., and the atmosphere is at the same time heavily charged with moisture. When a specific gravity bottle is filled with a liquid at 15·5 centigrade, and the stopper with a capillary bore is inserted, the bottle cannot be at once weighed, on account of the extent to which water has been condensed upon the surface of the bottle. By the time the temperatures of the balance case and of the liquid have become equalised, the latter will have expanded, and a not inconsiderable proportion of it will have escaped.

The author has devised a method of avoiding this source of error. His rules for testing spirits will be found well adapted for use in tropical climates. The accompanying tables have been specially re-calculated by Babu Güindra Nath Bose.

Dr. Warden points out the advantage of having in a set of decimal weights pieces for 3, 0·3, and 0·03 grm.

*The Mineral Industry, its Statistics, Technology, and Trade, in the United States and other countries from the Earliest Times to the end of* 1892. Vol. i. Edited by R. P. Rothwell. New York: The Scientific Publishing Company.

This most useful work is designated as the "Statistical Supplement of the *Engineering and Mining Journal.*" The compilation has been chiefly made with a view to American conditions and exigencies. Nevertheless, the mining industries of the whole world are fairly and, in general, very fully described.

The editor, in his preface, apologises for the retention of the English system—or unsystem?—of weights and measures. But in his denunciation he forgets the two causes which have, so far, delayed the introduction of the metric system into Britain. The first of these is the polysyllabic nomenclature which the French innovators sought to impose upon the world in their rage for everything classical. Had the various denominations of the metric system received monosyllabic names, it would have met with much more general acceptance in our midst. The second obstacle is the reluctance of the English people to be dictated to. The general use of the new weights and measures could only be enforced by a system of espionage and interference which might easily overthrow a ministry. But we submit that nations which persist in the use of Baumé's hydrometer scale have little room to take up their parable against us.

It will be seen that, in addition to mining and metallurgy, this work embraces in its scope some of the most important chemical manufactures, such as cements, alkali, bleaching powders, manures, salts of chromium, &c.

The author very justly denounces the Cornish copper assay. But he admits that there is no small difficulty in changing a system which for more than a century has been at the foundation of all business in this department. The difficulty is likely to diminish from the circumstance that the yield of the copper mines in the United Kingdom has greatly fallen off.

Mica-mining is said to have greatly fallen off owing to the large imports from India, which, despite the McKinley tariff of 35 per cent, undersell the American product.

In the production of asbestos Canada leads the world, and its produce is largely sold, even in Italy, close to the mines of that country.

Common salt is less fully noticed than most useful minerals. Save in the form of statistical tables, the salt deposits of England, Prussia, Galicia, and North Western India receive very scanty notice.

Phosphatic minerals are "under a cloud," owing to the depressed state of agriculture in many parts of Europe. The output of coprolites in England, from 262,382 tons as raised in 1876, has fallen to 10,164 tons.

Concerning mercury the intelligence is not cheering. The rumours of heavy veins of cinnabar having been traced in Mashona Land have no foundation.

In the production of nickel Canada seems to be gaining ground on New Caledonia. The yields from Norway and the United States are decreasing.

In speaking of graphite no particulars are given concerning the yields from Ceylon, Siberia, and Norway, the last-mentioned being very low in quality.

This work will meet with a large demand among miners, metallurgists, and consumers of or dealers in metals.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 24, June 12, 1893.

**The Heat of Combustion of the Principal Gaseous Hydrocarbons.**—MM. Berthelot and Matignon.—A thermo-chemical paper, in which the authors utilise the most recent determinations made by means of compressed oxygen in the calorimetric bomb.

At the meeting of the Academy on June 12th Professor Baron Nordenskiold was elected a foreign associate, *vice* the late Prof. Decandolle.

**The Photographic Properties of the Salts of Cobalt.**—Auguste and Louis Lumière.—The authors have previously shown that cobaltic oxide is rapidly reduced to a cobaltous salt if exposed to light in presence of organic matter. They have utilised this property for producing photograpic images by treating the papers exposed to light under a suitable proof by reagents which differentiate the cobaltous and the cobaltic salt. For this purpose they find potassium ferricyanide very suitable.

**Atomic Weights of Stas.**—J. D. Van der Plaats.—The author refutes the hostile criticisms of Henrichs, who has alleged that "the celebrated analyses of Stas contain systematic errors, on account of which they cannot be retained in chemistry, and that all the atomic weights of Stas are inaccurate, and that all the scientific conclusions founded upon the fictitious accuracy of these data ought to disappear." The author remarks that the chemistry of precision is a science of the laboratory, and has nothing in common with the art of associating figures.

**On Chromodisulphuric, Chromotrisulphuric, and Chromosulphochromic Acids.**—A. Recoura.—The author studies two new acids having properties analogous to those of chromosulphuric acid. One of them, chromodisulphuric acid, is derived from the combination of 1 mol. green chromium sulphate with 2 mols. of sulphuric acid. It is a tetrabasic acid, $(Cr_25SO_4)H_4$. Chromotrisulphuric acid is formed by the combination of 1 mol. green chromium sulphate with 3 mols. sulphuric acid; it is a hexabasic acid, $(Cr_26SO_4)H_6$. The three acids have the appearance of deep green powders, soluble in water in all proportions. In the solid state they are perfectly stable, but in solution they are rapidly split up into sulphuric acid and chromium sulphate. Chromosulphochromic acid has the composition $Cr_23SO_4,CrO_4H_2$.

**Action of Oxygen upon Sod-ammonium and Potass-ammonium.**—A. Joannes.—The author has continued his researches on the ammoniums formed by the alkaline metals, and has studied their behaviour with different gases. With pure dry oxygen the liquid becomes of a black-blue, which grows paler in proportion as the alkaline ammonium disappears.

**On Soft Sulphur Tempered in the State of Vapour.**—Jules Gal.—The distillation of iron pyrites yields sulphur, which condenses on the surface of the water in elastic plates, containing from 60 to 70 per cent of insoluble sulphur.

**Determination of Manganese by Oxydimetric Methods.**—Adolphe Carnot.—This paper will be inserted in full.

**On the Product of Asymmetry.**—Ph. A. Guye.—A purely mathematical paper, incapable of useful abstraction.

**Alcoholic Fermentation of Jerusalem Artichokes under the Influence of Pure Yeasts.**—Lucien Lévy.—The author has used a yeast of the Romané Conti grape, and has obtained a spirit of good flavour, containing very little light alcohol.

**A New Series of Colouring Substances.**—M. A. Trillat.—It may be concluded, from the author's experiments, that formaldehyd reacts readily upon those aromatic amines, simple or compound, in which one hydrogen of the nitrogen group is available. The shade of the amidated colouring matters is profoundly modified by this substitution. In general it proceeds from the left towards the right in the series of spectral colours.

**The Assimilation of the Gaseous Nitrogen of the Atmosphere by Microbia.**—S. Winogradsky.—The author, at the conclusion of his paper, raises the following questions:—Is there a constant proportion between the quantity of sugar decomposed and the nitrogen assimilated? Can the assimilation be effected at the expense of other organic substances beside sugar, those especially which are found in the soil? What are the conditions of cultivation most favourable to the gain of nitrogen?

**Oil of the Eggs of the Algerine Cricket (*Acridium peregrinum*).**—Raphael Dubois.—This oil contains 1·92 per cent by weight of phosphoric anhydride. One kilo. of fresh eggs yields from 40 to 50 grms. of the oils. It is suggested that the oil may be utilised both therapeutically and industrially.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 11.

**Determination of Phosphorus in Irons and Steels.**—Adolphe Carnot.—Already inserted.

**Determination of Phosphorus in Vegetable Soils.**—Adolphe Carnot.

**Determination of Hydrosulphocyanic, Hydrocyanic, and Hydrochloric Acids.**—P. L. Jumeau.—To be inserted in full.

**Liquid Chlorine.**—M. Fribourg.—Liquefied chlorine is now produced at the works of Pechiny, at Salindres, and is sent out in cylinders of iron, which are not attacked by anhydrous chlorine. Each such cylinder contains 50 kilos. = 15,000 litres of gaseous chlorine.

**Metaldehyd.**—C. Friedel.—A stereo-chemical study.

**A Novel Method of Preparing Acrylic Acid (Propenoic Acid).**—C. Moreau.—This lengthy memoir does not admit of useful abstraction.

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## THE ASSAY OF MANGANESE OXIDES WITH HYDROGEN PEROXIDE.

By ADOLPHE CARNOT.

It is known that oxygenated water is decomposed with effervescence in contact with manganese peroxide, and that a small quantity of this oxide suffices to destroy an indefinite quantity of oxygenated water.

It is not the same when the peroxide and the oxygenated water are in presence of an acid, even if very dilute or weak, but capable of combining with manganous oxide. There occurs then a simultaneous decomposition of the two peroxides, and the quantity of oxygen liberated is exactly double that which exists in the manganese peroxide over and above MnO.

This reaction occurs readily, even in the cold, whether with nitric or sulphuric acid (very dilute), or with acetic acid as long as none of these acids attacks $MnO_2$. It is explained in the same manner as many other simultaneous and correlative decompositions, the mechanism of which has been explained by M. Berthelot.

The final transformation is expressed for manganese peroxide by the following formula:—

$$MnO_2+HO_2+NO_5HO=MnO,NO_5+2HO+O_2.$$

It occurs similarly for the red ignited oxide, $Mn_3O_4$:—

$$Mn_3O_4+HO_2+3(NO_5,HO)=3(MnONO_5)+4HO+O_2.$$

It is also verified exactly for the oxide precipitated by oxygenated water and ammonia in excess containing, as I have shown, 5 equivalents of available oxygen to 6 equivalents of manganese, $Mn_6O_{11}$:—

$$Mn_6O_{11}+5HO_2+6(NO_5,HO)=$$
$$=6(MnO,NO_5)+H\ HO+O_{10}.$$

After having satisfied myself of the perfect exactitude of the relations indicated, I sought to deduce from them a practical process for the determination of the *available oxygen* in the higher oxides of the manganese; or what is often called the commercial assay of the ores of manganese, collecting and measuring over water the gas evolved.

The arrangement adopted is very simple.

We fix on a support with clamps a small flask of the capacity of about 150 c.c., having a caoutchouc stopper with two perforations. Through one of these passes a straight tube fitted with a funnel, or a phial with a glass cock, the point of which must descend to the bottom of the flask. The other aperture has a gas delivery-tube bent four times, ending in a graduated gas jar, filled with water and arranged on the trough. We introduce into the flask 1 grm. of the manganese oxide reduced to a fine powder, then about 30 c.c. of water, and 20 c.c. of nitric acid, which decomposes any carbonates present in the sample. We allow the carbonic acid to escape entirely; then we insert the stopper, leaving the cock open. We can then observe that not only the graduated jar, but also the delivery-tube is filled with water up to the point where it emerges from the water-trough.

We close the cock, pour into the funnel a measured volume of 20 c.c. oxygenated water, at 10 vols., then we cause it to flow gently into the flask, taking care to close the cock as soon as the last traces of oxygenated water have passed.

The action takes place at once without heat, and the escape of oxygen, which is at first very rapid, is completed in a few minutes if care is taken to shake the flask from time to time. Nothing then remains but to measure the volume of oxygen liberated.

To this end, it is sufficient to measure the increase of the total gaseous volume, ascertaining that the temperature and the pressure have remained the same as at the beginning of the experiment. The gas is lowered until the water is exactly at the same level within and without. The delivery-tube is withdrawn, and the volume of gas is read off, and brought anew exactly to the atmospheric pressure.

To find the total volume of oxygen liberated, or the increased volume of gas in the apparatus from the beginning to the end of the experiment, we must add to the volume, V, just read off the small volume of gas, $v$, which has filled the extremity of the delivery-tube originally full of water, a volume which is easily measured with water, once for all. On the other hand, we must deduct the volume, $v'$, of the oxygenated water which has been introduced into the flask and has displaced an equal volume of oxygen.

The total increase of the gaseous volume, $V_t$, is thus measured at the temperature, $t$, and the atmospheric pressure, H, observed at the outset. The gas is, moreover, saturated with moisture, the tension of which, $h$, is known according to the temperature.

Knowing that the weight of 1 litre of dry oxygen at 0° and at 760 m.m. is 1·4298 grm., and knowing the total volume, $V_t$, expressed in c.c., we calculate in grms. the weight, $p$, of available oxygen in 1 kilo. of ore by means of the formula:—

$$p=\tfrac{1}{2}V_t,\times 1{\cdot}4298\times\frac{H-h}{760}\times\frac{1}{1+0{\cdot}00367.t.}$$

—*Comptes Rendus*, cxvi., 1295.

## PREPARATION OF CERTAIN REFRACTORY METALS IN THE ELECTRIC FURNACE.

### Tungsten, Molybdenum, Vanadium.

By HENRI MOISSAN.

In this paper the author indicates the easy preparation of tungsten, and molybdenum, and vanadium carbides.

### *Tungsten.*

It is known that tungsten may be easily obtained in the form of a powder by reducing tungstic acid at a red heat in a current of hydrogen. The metallic powder thus obtained has hitherto been fused only with great difficulty. Desprez has succeeded in melting small quantities of tungsten in the arc produced by 200 Bunsen elements. In the flame of the oxyhydrogen blowpipe tungsten is quickly oxidised, and soon disappears in fumes of tungstic acid.

The preparation of tungsten, either pure or as a carbide, is easily effected in the electric furnace. The mixture of tungstic acid and coke is placed in the crucible of the furnace, and in about ten minutes, with a current of 350 ampères and 70 volts, we obtain a metallic regulus of about 120 grms. If we have taken care to add a great excess of oxide, we may obtain the pure metal in the first experiment; but it is preferable to prepare first a metal slightly carbised, which is much more fusible, and to remelt it in a second operation in presence of a large excess of tungstic acid. In this manner we obtain a brilliant metal, very hard, and of the specific gravity 18·7. If the carbon is in excess, we obtain cast metals of very varying compositions. Four specimens gave on analysis the following percentages of carbon:—0·64, 2·74, 4·56, and 6·33. These cast metals have a brilliant fracture. They are stable on exposure to air, and are sometimes covered with a fine layer of blue tungsten oxide.

This metal has the curious property of fixing a large proportion of carbon. If the preparation of tungsten has been made in presence of an excess of coke, with a current of 1000 ampères and 70 volts, we obtain cast metals much richer in carbon, specimens of which were found to contain C 17·27, 17·61, 18·27, and 18·81 per cent.

### *Molybdenum.*

Pure molybdenum has been regarded hitherto as infusible. Henri Debray had difficulty in melting with the oxyhydrogen blowpipe a molybdenum carbide containing from 4 to 5 per cent of carbon. In the electric furnace the operation requires only a few moments.

We set out with pure ammonium molybdate, which on ignition yields a grey pulverulent oxide. It is mixed with charred sugar, and heated for seven to eight minutes with a current of 350 ampères and 70 volts. We thus obtain a regulus of cast metal which is easily detached from the crucible. This molybdenum carbide is very hard, scratching glass and steel. The fracture is brilliant, and it is not affected by moist air. Its specific gravity is 8·6. Its composition is variable, according to the proportion of coke employed. The percentage of carbon ranged from 9·77 to 9·90.

### *Vanadium.*

The important researches of Roscoe proved the difficulty of obtaining this elementary substance. By reducing vanadic acid with coke there was merely obtained a silicide scarcely fusible at the temperature of a good blast furnace. Ultimately he surmounted the numerous difficulties which this preparation presented, and he obtained metallic vanadium by reducing vanadium bichloride with pure dry hydrogen. He remarks, however, that the powder of metal thus obtained still contains a trace of oxygen, and 1·3 per cent of hydrogen.

In the preparation of cast vanadium in the electric furnace we set out with pure ammonium meta-vanadate, which on ignition yielded an easily fusible vanadic oxide of a yellowish brown colour. It was mixed with the charcoal of sugar, and when placed at some centimetres distance from the arc produced by a current of 350 ampères and 70 volts no reduction occurred. It was necessary to let the arc play in contact with the powder for twenty minutes, and then we only obtained on the surface of the mixture small metallic granules of the size of a lentil.

On employing an arc produced by a current at 1000 ampères and 70 volts, we obtained the complete reduction of the oxide, by the fusion of the carbide, in a few moments. The cast metals obtained under these conditions contained respectively C 25·47, 25·65, and 17·56.

It is a curious fact that as the temperature rises, we tend towards metallic carbides very rich in carbon.

The vanadium carbide has the specific gravity 5·3.

It appears from these experiments that pure chromium is more infusible than platinum, whilst higher than chromium we must place molybdenum, uranium, tungsten, and lastly vanadium.—*Comptes Rendus*, cxvi., p. 1225.

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## THE VOLATILISATION OF SILICA AND ZIRCONIA, AND THE REDUCTION OF THESE SUBSTANCES BY CARBON.

By HENRI MOISSAN.

On submitting zirconia to the high temperature of the electric furnace, this oxide quickly enters into fusion. After the lapse of ten minutes, on operating with a current of 360 ampères, and 70 volts, there appear very abundant white fumes. These fumes consist of the vapour of zirconia, which earth at this high temperature is in full ebullition. If the vapours are condensed upon a cold substance we obtain a white powder, which is treated with very dilute hydrochloric acid to remove any lime present. After washing with boiling distilled water and desiccation there remains a white powder, which under the microscope appears as white rounded masses, without any transparent particles. This powder presents all the characters of zirconia. It scratches glass with ease, and its sp. gr. is 5·10.

After cooling, there remains in the crucible a mass of melted zirconia, with a crystalline fracture. Within the furnace, in the cooler parts, we sometimes find characteristic crystals of zirconia, of the form of transparent dendrites, of a vitreous lustre, not attacked by sulphuric acid, and capable of scratching glass.

This zirconia, when in fusion, is easily reduced by coke. If we place a quantity of zircon in a crucible of coke, we find below the residue of melted zirconia a metallic regulus of zirconium, containing neither carbon nor nitrogen, but containing variable quantities of zirconia.

On the contrary, on mixing zirconia with an excess of coke, we obtain a substance of a metallic appearance, not containing nitrogen, and which on analysis gave the following results:—

| | 1. | 2. | 3. |
|---|---|---|---|
| Carbon .. .. | 4·22 | 4·60 | 5·10. |

When the zirconium carbide is richer in carbon it is rapidly destroyed on exposure to the air.

This carbide may be refined so as to yield metallic zirconium by re-melting in presence of an excess of liquid zirconia. Zirconium is a very hard body, which easily scratches glass and ruby, Its sp. gr. is 4·25. It therefore approximates very closely to that of Troost's zirconium (4·15).

*Silica.*—Fragments of rock crystal in a crucible of coke were exposed to the action of the electric arc produced by a current of 350 ampères and 70 volts. In a few moments the silica enters into fusion, and in seven or eight minutes ebullition sets in.

There then issues from the furnace, by the apertures which give passage to the electrodes, a smoke of a bluish colour, lighter than that produced by zirconia. These vapours are given off plentifully as long as the experiment continues. They may be condensed by placing an inverted crystalliser at some distance from the apertures of the furnace. The interior of this crystalliser is rapidly coated with a slight layer of a scarcely transparent substance, of a slightly bluish white colour. On taking up the contents of the crystalliser in water, and examining this residue under the microscope with a very low power, we see that it is chiefly formed of opalescent spheres, quickly soluble in hydrofluoric acid. These small spheres of silica, visible to the naked eye, are solid. They sometimes present at one point a hollow, which seems to indicate that the melted silica has contracted in volume in passing from the liquid to the solid state. Along with these spheres there are numerous particles of amorphous silica.

If we wish to collect a notable quantity of this product it is better to use a furnace the cover of which has an aperture for the escape of the vapour of silica. A glass bell is placed over this aperture, and we may thus, in from ten to fifteen minutes, collect 20 grms. of a very light white powder, which is purified from lime by washing with dilute hydrochloric acid.

The form of the condensed silica depends of course on the more or less rapid refrigeration of the vapour. This process must not be too rapid if we wish to obtain numerous spherules of silica.

This silica is very soluble in hydrofluoric acid. It dissolves in the cold with a slight rustling noise. It is readily attacked by melting potassium hydrate and by alkaline carbonates. Its sp. gr. is 2·4, *i. e.*, a little lower than that of rock crystal. The spherules scratch glass with ease.

On studying the deposit formed in glass globes in which the electric arc has been caused to play for lighting, we have found small globules of silica identical with those just described. The opalescence of glass globes in which the arc has been in action for some time is therefore due to the volatilisation of silica. This silica is derived from the impurities of the electric carbons.

We will add that silica at this temperature is easily reduced by carbon, and yields a crystalline silicon carbide which we are further examining.—*Comptes Rendus*, cxvi., p. 1222.

## ON AMIDOPHOSPHORIC ACID.*

By H. N. STOKES.

(Continued from p. 11).

*Acid sodium amidophosphate*, $\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{ONa}\\ \mathrm{OH}\end{matrix}+x\mathrm{H_2O}$ (?). — This is prepared by boiling the ether ten minutes with strong caustic soda, cooling and acidifying with acetic acid. It separates at once without adding alcohol as a crystalline powder, which is washed with dilute alcohol, dissolved in ammonia, and re-precipitated by acetic acid or carbon dioxide. It forms a heavy sandy powder, consisting of well-defined crystals belonging to the hexagonal system, occurring sometimes as hexagonal plates or prisms without pyramids, occasionally as very symmetrical double pyramids without prism surfaces. It is scarcely soluble in cold water, insoluble in alcohol. If boiled with water it dissolves, and is at once converted into acid sodium ammonium phosphate; the same change occurs slowly at ordinary temperature under water. Like all other amidophosphates, it is instantly converted into phosphoric acid by warm dilute acids. On ignition it loses ammonia, and leaves a vitreous residue of sodium hexametaphosphate. It contains small but varying amounts of water. The analysis of one preparation gave—

| | Calculated for $\mathrm{PO.NH_2.ONa.OH}+\frac{1}{4}\mathrm{H_2O}$. | | Found. | |
|---|---|---|---|---|
| P | 25·11 | | 25·08 | |
| N | 11·36 | 11·49 | | 11·34 |
| Residue ($\mathrm{NaPO_3}$) | 82·54 | | 82·43 | |

Other samples contained less water. This water is accounted for in part by the presence of a small amount of acid sodium ammonium phosphate; but the latter, when determined as in the acid potassium salt, was found to be only 2 to 2·5 per cent, while the whole amount of water present, if assumed to be in the form of ammonium salt. would make the amount 16·8 per cent. The water is therefore present mainly as such. It does not act on the amido group at 100°, as the quantity of ammonia expelled by alkali after heating at this temperature is not increased, and there is no loss of weight. At 150° it reacts, converting a portion of amide into ammonium salt, which at the same time loses ammonia, the residue being found to contain less nitrogen. The acid sodium salt dissolves rather difficultly in excess of ammonia, probably forming the sodium ammonium salt; from this solution it is re-precipitated by carbon dioxide, or even by expelling the ammonia by an air current or spontaneous evaporation. In this respect it resembles the neutral phosphates containing ammonia.

*Neutral sodium amidophosphate*, $\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{(ONa)_2}\end{matrix}$, is readily made by treating caustic soda solution with excess of acid salt, the excess remaining undissolved. It forms bunches of needles or prisms, extremely soluble in water, but not deliquescent. By the action of carbon dioxide, even that in the air, it is decomposed into acid salt and sodium carbonate. Alcohol precipitates it as a syrup from aqueous solution.

*Acid lithium amidophosphate* is precipitated by lithium chloride from a strong solution of the acid potassium salt, in the form of difficultly soluble crystalline granules. On boiling it is converted into phosphates of lithium.

*Acid ammonium amidophosphate* is formed by decomposing either the acid or neutral silver salt with ammonium sulphide and precipitating by alcohol. It forms a beautiful network of needles, crossing at angles of 60°, and is very soluble in water and permanent in the air. As it is formed by precipitating an ammoniacal solution by alcohol, it appears that the neutral salt is very unstable, if capable of existence.

*Potassium ammonium amidophosphate* is precipitated by alcohol from an ammoniacal solution of the acid potassium salt as a syrup, which is decomposed by washing with alcohol into acid potassium salt and ammonia.

*Acid hydroxylamine amidophosphate*, obtained by precipitating a moderately strong solution of the acid potassium salt with hydroxylamine hydrochlorate, is difficultly soluble in water, and forms brilliant rhombic plates and prisms. Its crystallising power is greater than that of any other salt obtained. A neutral salt could not be prepared.

The preparation of salts of the earths and heavy metals from the acid potassium salt is interfered with by the latter being contaminated with a small amount of phosphate. The contamination of the precipitate in the case of the salts is best avoided by adding to the ice-cold solution of the acid potassium salt, before precipitation, a very little dilute nitric acid, which effectively holds all phosphate in solution. In making neutral salts it is not so easy to get rid of the phosphate; the ways in which this was accomplished are given in special cases below.

*Acid barium amidophosphate*, $\left(\begin{matrix}\mathrm{NH_2}\\ \mathrm{PO{\cdot}OH}\\ \mathrm{O—}\end{matrix}\right)_2\mathrm{Ba}+2\frac{1}{2}\mathrm{H_2O}$, is obtained by adding to an ice-cold solution of acid potassium salt, faintly acidified with nitric acid, barium chloride in excess. It thus forms a supersaturated solution, which crystallises only on rubbing with a glass rod. The precipitate is washed with a little water and alcohol. It forms groups of radiating microscopic plates, and once formed is quite difficultly soluble in water. On boiling its solution, a scaly crystalline precipitate of acid barium phosphate, $\mathrm{BaHPO_4}$, at once forms. It contains about 2½ mols. crystal water, the greater part of which is lost at 100°; but this cannot be directly determined, owing to its tendency to pass into ammonium salt with loss of ammonia. On ignition it fuses to a glass of barium hexameta-phosphate.

| | Calculated for $\mathrm{Ba(PO_3NH_2)_2}+2\frac{1}{2}\mathrm{H_2O}$. | Found. |
|---|---|---|
| Loss ($2\mathrm{NH_3}2\frac{1}{2}+\mathrm{H_2O}$) | 20·17 | 19·82 |

The residue gave—

| | Calculated for $\mathrm{Ba(PO_3)_2}$. | Found. |
|---|---|---|
| Ba | 46·43 | 47·12 |
| P | 21·03 | 21·38 |

*Neutral barium amidophosphate*, $\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\mathrm{Ba}\end{matrix}+\mathrm{H_2O}$.—By mixing a dilute solution of acid potassium salt with ammoniacal barium chloride solution, and filtering quickly from the small amorphous precipitate of barium phosphate, the salt soon crystallises. It forms very characteristic hard and brittle rhombic plates, often with truncated angles, often superposed in coincident or partly turned position, sometimes also as fine prisms with many sharply defined faces. It is unchanged at 100°, but at 150° the crystal water is taken up to form ammonium salt, which at once loses ammonia, forming acid barium phosphate, which on ignition leaves a residue of pyrophosphate, giving off but little ammonia.

| | Calculated for $\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\mathrm{Ba}\end{matrix}+\mathrm{H_2O}$. | Found. |
|---|---|---|
| Loss of 1 mol. $\mathrm{NH_3}$ at 150° | 6·80 | 6·84 |
| Total loss on ignition, $\mathrm{NH_3}+\frac{1}{2}\mathrm{H_2O}$ | 10·40 | 10·70 |

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* *American Chemical Journal*, vol. xv., No. 3.

The residue gave—

| | Calculated for $Ba_2P_2O_7$. | Found. |
|---|---|---|
| Ba | 61·17 | 61·80 |
| P | 13·84 | 14·44 |

The salt is very difficultly soluble in water. Its solution, or the liquid from which it has not yet crystallised, gives on boiling, even in the presence of an excess of ammoniacal barium chloride, a scaly precipitate of acid barium phosphate.

| | Calculated for $BaHPO_4$. | Found. |
|---|---|---|
| Loss on ignition $\frac{1}{2}H_2O$ | 3·86 | 4·65 |

The residue gave—

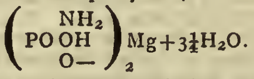
| | Calculated for $Ba_2P_2O_7$. | Found. |
|---|---|---|
| Ba | 61·16 | 61·76 |

The salt shows a peculiar behaviour when formed in the presence of strong ammonia. By mixing a solution of the acid potassium salt with strongly ammoniacal barium chloride, an amorphous precipitate is formed, which dissolves (excepting traces of phosphate) on adding water. Strong ammonia re-precipitates it, and more water dissolves it; this process may be repeated several times. The solution soon deposits crystals of the neutral salt, and the precipitate itself soon turns to scales of the same substance. Filtered off and washed with ammonia, it gave on analysis figures corresponding to those of the neutral salt.

*Acid calcium amidophosphate*, obtained like the barium salt, is much less soluble than the latter, and forms spherical aggregations of needles.

*Neutral calcium amidophosphate* is formed like the neutral barium salt, but is much less soluble. Its crystallising power is also much less. From very dilute solutions it separates gradually in the form of microscopic groups of flat-pointed prisms; from concentrated solutions as an amorphous precipitate which does not become crystalline, while from solutions of intermediate strength it is at first amorphous, but gradually becomes crystalline.

*Acid magnesium amidophosphate*,—



$$\left(\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{OH}\\ \mathrm{O-}\end{matrix}\right)_2\mathrm{Mg}+3\tfrac{1}{2}\mathrm{H_2O}.$$

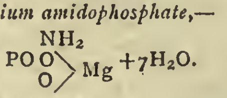
On mixing an ice-cold strong solution of acid potassium salt, acidified slightly with nitric acid, with magnesium chloride, nothing separates, even after many hours. On rubbing with a glass rod, crystallisation starts at once. Once separated it is almost insoluble in water, and forms microscopic granules consisting of radiating needles or prisms. It is insoluble in ammonium chloride. At 100° it retains 2 mols. water; on ignition it gives off ammonia and water, and leaves magnesium metaphosphate.

| | Calculated for $Mg(PO_3NH_3)_2+3\frac{1}{4}H_2O$. | Found. |
|---|---|---|
| Loss $(2NH_3+3\frac{1}{4}H_2O)$ | 33·71 | 33·86 |

The residue gave—

| | Calculated for $Mg(PO_3)_2$. | Found. |
|---|---|---|
| Mg | 13·18 | 12·85 |
| P | 34·10 | 33·88 |

*Neutral magnesium amidophosphate*,—



$$\mathrm{PO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\!\!>\mathrm{Mg}+7\mathrm{H_2O}.$$

This salt has the same empirical composition as crystallised ammonium magnesium phosphate,—

$$MgNH_4PO_4+6H_2O,$$

but differs entirely in its properties. It forms at once on adding magnesia mixture to a solution of acid potassium salt, or, better, by precipitating neutral sodium salt with a magnesium salt. Any phosphoric acid present is first thrown down by a little of the precipitant, either as magnesium or magnesium ammonium phosphate; even when phosphoric acid is in excess it is completely thrown down by magnesia mixture before any amidophosphate forms, and the change can easily be followed by observing the crystals under the microscope. From solutions containing ammonium chloride (as when magnesia mixture is used) it crystallises in very characteristic plates, often nearly rectangular, but more frequently with truncated angles, forming oblong octagonal plates. In the absence of ammonium salts it forms thick prisms, in either case easily distinguishable from ammonium magnesium phosphate. It is difficultly but perceptibly soluble in water, and quite readily in dilute ammonium chloride solution, and may be separated from any accompanying ammonium magnesium phosphate in this way. From its aqueous solution ammonia precipitates magnesium hydroxide. On boiling its aqueous solution, ammonium magnesium phosphate is at once formed. It dissolves in acetic acid; from its solution in nitric acid, alcohol precipitates acid salt. Even when free from ammonium salt, caustic potash causes more or less evolution of ammonia in the cold. Over sulphuric acid it quickly loses most of its crystal water, but the last two or three molecules are given off very slowly, and constant weight could not be obtained. At 100° it loses somewhat more than 5 mols., but this cannot be accurately determined, as at this temperature partial decomposition of the amide with loss of ammonia occurs, as shown by analysis of the residue. On ignition it leaves magnesium pyrophosphate.

| | Calculated for $MgPO_3NH_2+7H_2O$. | Found. | |
|---|---|---|---|
| P | 12·67 | 12·59 | |
| N | 5·73 | 6·53 | 6·27 |
| Mg | 9·79 | 9·77 | |
| Loss on ignition | 54·70 | 54·79 | |

*Acid, manganese amidophosphate*, prepared like the acid magnesium salt, forms faintly pinkish microscopic crystals, or granular and lenticular forms. It contains crystal water, is difficultly soluble, and shows no tendency to form supersaturated solutions.

*Neutral manganese amidophosphate*, from the neutral sodium salt, is an amorphous white precipitate.

*Acid zinc amidophosphate* is difficultly soluble in water; soluble in acetic acid and in ammonia. It crystallises readily in small but finely-formed rhombic prisms with pyramids, or in hexagonal plates.

*Neutral zinc amidophosphate* is an amorphous white precipitate, perceptibly soluble in water. Both salts are converted into phosphate by boiling.

*Cobalt amidophosphates.* The *acid* salt forms readily from the acid potassium salt with a cobalt salt, after adding a drop of nitric acid. It is difficultly soluble in water; soluble in ammonia, and forms pink granules. The *neutral* salt is an amorphous pink precipitate.

*Nickel amidophosphates.* The *acid* salt has a great tendency to supersaturation, and can only with great difficulty be made to crystallise. Once formed, it consists of minute crystalline granules, difficultly soluble in water. The *neutral* salt is an amorphous, nearly colourless precipitate, soluble in acetic acid and in ammonia.

*Ferrous amidophosphates.* The *acid* salt, formed as above, crystallises very readily in nearly colourless microscopic crystals, apparently of the regular system, and consisting of the dodekahedron or combinations of cube and octahedron. It is nearly insoluble in water or ammonium chloride; soluble in ammonia. The *neutral* salt is a dirty greenish, amorphous precipitate, soluble in much water, in acetic acid, and in ammonia.

*Ferric amidophosphates.* Both acid and neutral alkali salts give, with a neutral solution of ferric chloride, white, amorphous precipitates, soluble in excess of amidophosphate and in ammonia, insoluble in acetic acid.

*Aluminium amidophosphate.* Neutral sodium salt gives, with alum, a white, amorphous precipitate, completely soluble in ammonia.

*Chromic amidophosphate*, from neutral sodium salt, is a very nearly colourless amorphous precipitate, soluble in ammonia on warming.

*Cupric amidophosphates.* The *acid* salt crystallises in rosettes and dumb-bell-like forms, nearly insoluble in water. The *neutral* salt is an amorphous precipitate, slightly soluble in water, and converted into phosphate by boiling.

*Mercuric amidophosphates.* Neither acid nor neutral salts are precipitated by mercuric chloride. On boiling, mercuric phosphate is formed.

*Cadmium amidophosphates.* By mixing solutions of acid potassium amidophosphate and cadmium chloride, crystalline precipitates somewhat soluble in water are obtained. These differ in form according as one or the other reagent is in excess; with excess of cadmium chloride a double salt is formed, which gives off ammonium chloride on heating.

*Lead amidophosphate.* Acid potassium salt and lead acetate give a precipitate consisting of groups of radiating plates, slightly soluble in water, presumably acid salt.

(To be continued).

## THE DEPOSITS OF NATIVE SODA, NEAR LARAMIE, WYOMING.*

By H. PEMBERTON, Jun., and GEO. P. TUCKER.

Previous to the Civil War, and at a time when the line of civilisation extended as far only as the Mississippi River, very little was known of the part of the United States west of that limit. A vast region now comprising many large States was described in the geographies of the day as "the great American Desert." It constituted a part of the prairies or plains, so often mentioned in Cooper's novels. And while the prairies, as a general rule (and particularly in elevations not much above sea-level), are composed of a fertile and rich soil, their character changes as the approach is made to the Rocky Mountains, and when an elevation of 7000 feet is reached, as in Wyoming, the soil and climate resemble somewhat the soil and climate of Nevada and other parts of the Great Basin. On this high Wyoming plateau, particularly in the neighbourhood of the town of Laramie, one drives for miles over a perfectly flat country, with nothing but some distant hills to break the wide circle of the horizon—not even a single tree. A little thin grass grows in the gravelly soil, but no other form of vegetation, except when aided by irrigation. The region is nearly rainless, the relative humidity quite low, and all conditions favourable to the formation of the saline deposits peculiar to this portion of the United States.

About fourteen miles south-west of Laramie, there exists a deposit of sulphate of soda; such deposits are locally known as "lakes." The deposit in question is composed of three of these lakes lying within a stone's throw of one another. They have a total area of about sixty-five acres, the local names of the three being the Big Lake, the Track Lake, and the Red Lake. They are the property of the Union Pacific Railroad Company, are connected by a branch of that road with the main line at Laramie, and are generally known as the Union Pacific lakes.

In these lakes the sulphate of soda occurs in two bodies or layers. The lower part constituting the great bulk of the deposit, is a mass of crystals of a faint greenish colour, mixed with a considerable amount of black slimy mud. It is known as the "solid soda." We give an analysis of this below.

This solid soda is stated to have a depth of some 20 or 30 feet. Borings were made a number of years ago under the direction of the Union Pacific Railroad agents, but all attempts to obtain the results of the same were futile, as the records have been mislaid or lost. There is nothing to prove that the depth is not shallower than stated above.

*Analysis of Solid Soda immediately under the Top Layer of White Sulphate of Soda on Red Lake and Track Lake (U. P. Lakes).*

| | Anhydrous. Per cent. | Crystallised. Per cent. |
|---|---|---|
| $Na_2SO_4$ .. .. .. .. .. | 36·00 | 81·63 |
| $CaSO_4$ .. .. .. .. .. | 1·45 | 1·82 |
| $MgCl_2$ .. .. .. .. .. | 0·77 | 1·64 |
| NaCl .. .. .. .. .. | 0·21 | 0·21 |
| | 38·43 | 85·30 |
| Insoluble residue (at 100° C.) | | 13·86 |
| | | 99·16 |

Total chloride calculated as NaCl = 1·16 per cent.
This calculated on 100 parts anhydrous: $Na_2SO_4$ equals 3·22 per cent NaCl.

Above the solid soda occurs the superficial layer of *pure white crystallised sulphate of soda.* This is formed by solution in water of the upper part of the lower body—the crystals being deposited by evaporation or by cooling, or by the two combined. A little rain in the spring and autumn furnishes this water, as do also innumerable small sluggishly flowing springs present in all the lakes. But on account of the dry air of this arid region, the surface is generally dry or nearly so, and in midsummer the white clouds of efflorescent sulphate that are whirled up by the ever-blowing winds of Wyoming can be seen for miles. Even should there be a little water present, there is no difficulty in gathering the crystals by the train-load. The spring, however, is the worst season of the year, on account of the warm weather and of the rains—conditions unfavourable to the formation of crystals. The layer of this white sulphate is from 3 to 12 inches in thickness. When the crystals are removed, the part laid bare is soon replenished by a new crop.

The following is an analysis of the purest of this white sulphate of soda, calculated upon an anhydrous basis; that being the condition, of course, in which it would be used:—

| | |
|---|---|
| $Na_2SO_4$.. .. .. .. | 99·73 |
| $MgCl_2$ .. .. .. .. | 0·26 |
| Insoluble .. .. .. | trace |
| | 99·99 |

Several hundred tons of this have been shipped by the railroad to the works at Laramie City. The plant there for dehydrating the crystals is not of the best, and the long exposure to the dust and smoke of the fire gases in the evaporation—and again in the calcining—introduces more or less impurity into the finished calcined sulphate of soda. The following is an analysis of the latter:—

| | Finished calcined sulphate of soda. (From U. P. Lakes). | |
|---|---|---|
| $Na_2SO_4$ .. .. .. | 95·80 | soluble in water. |
| $CaSO_4$ .. .. .. | 0·76 | |
| NaCl .. .. .. | 1·84 | |
| Ignition .. .. .. | 0·19 | insoluble in water. |
| $SiO_2$ .. .. .. .. | 1·48 | |
| $Fe_2O_3$ .. .. .. | 0·06 | |
| $Al_2O_3$ .. .. .. | 0·31 | |
| CaO .. .. .. .. | 0·20 | |
| MgO.. .. .. .. | 0·44 | |
| | 101·08 | |

This analysis represents the general run of the sulphate, as manufactured in Laramie. The sample was taken from a carload lot sold to the Wyoming Glass Company.

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* Read before the Chemical Section of the Franklin Institute.

It contains only a trace of iron, and, of course, no free acid.

At the time when we examined these lakes, in 1888, they were entirely under water. An irrigating canal—or "ditch"—had been located within a half mile of them, the water from which had gradually collected to the extent of several feet in the lakes. The course of the canal has since been changed, and the lakes are again in about their normal condition.

Samples of this water were collected by us, and analysed as giving a very fair idea of the average composition of the deposits. The ingredients are calculated to the anhydrous condition. The last item, it will be noticed, is given as anhydrous borax, $Na_2B_4O_7$. It represents the results of titration with standard acid, using methyl-orange as an indicator. It may be noted that, on account of the lime salts present in solution, alkaline carbonates and phosphates must be absent, and direct test proved the absence of soluble silicates. We have noticed the same titration reaction (if we may so call it) in a sample of sulphate of soda from a deposit near Rawlins, Wyoming, and, in general, it may be stated that the character of the climate, soil, and formation in Wyoming is very similar to that of such parts of the Pacific Slope as are known to contain deposits of borax.

*Water from Big Lake (U. P. Lakes).*

Density $= 9\frac{3}{4}$° Tw. ($=$ 1·0487 sp. gr.).

10 c.c. contains:—

| | Grms. | | Per cent. |
|---|---|---|---|
| $Na_2SO_4$ .. .. .. .. .. .. | 0·4490 | = | 81·43 |
| $CaSO_4$ .. .. .. .. .. .. | 0·0175 | = | 3·17 |
| $MgSO_4$ .. .. .. .. .. .. | 0·0060 | = | 1·09 |
| $MgCl_2$ .. .. .. .. .. .. | 0·0643 | = | 11·66 |
| $Na_2B_4O_7$ ? .. .. .. .. .. | 0·0146 | = | 2·65 |
| Total solids .. .. .. .. | 0·5514 | | 100·00 |
| (Total solids by evaporation | 0·5417) | | |

One cubic foot contains $6\frac{36}{100}$ pounds of pure crystallised sulphate of soda.

*Water from Track Lake (U. P. Lakes).*

Density $= 14\frac{1}{2}$° Tw. ($=$ 1·0725 sp. gr.).

10 c.c. contains:—

| | Grms. | | Per cent. |
|---|---|---|---|
| $Na_2SO_4$ .. .. .. .. .. .. | 0·7563 | = | 92·23 |
| $CaSO_4$ .. .. .. .. .. .. | 0·0146 | = | 1·79 |
| $MgSO_4$ .. .. .. .. .. .. | 0·0070 | = | 0·85 |
| $MgCl_2$ .. .. .. .. .. .. | 0 0300 | = | 3·66 |
| $Na_2B_4O_7$ ? .. .. .. .. .. | 0·0121 | = | 1·47 |
| Total solids .. .. .. .. | 0·8200 | | 100·00 |
| Total solids by evaporation | 0·8240 | | |

One cubic foot of this water contains $10\frac{72}{100}$ pounds of pure crystallised sulphate of soda.

*Water from Red Lake (U. P. Lakes).*

Density $= 17\frac{3}{4}$° Tw. ($=$ 1·0887 sp. gr.).

10 c.c. contains:—

| | Grms. | | Per cent. |
|---|---|---|---|
| $Na_2SO_4$ .. .. .. .. .. .. | 0·9307 | = | 91·77 |
| $CaSO_4$ .. .. .. .. .. .. | 0·0201 | = | 1·98 |
| $MgSO_4$ .. .. .. .. .. .. | 0·0143 | = | 1·41 |
| $MgCl_2$ .. .. .. .. .. .. | 0·0416 | = | 4·10 |
| $Na_2B_4O_7$ ? .. .. .. .. .. | 0·0075 | = | 0·74 |
| Total solids .. .. .. .. | 1·0142 | | 100·00 |
| Total solids by evaporation | 1·0320 | | |

One cubic foot of this water contains $13\frac{19}{100}$ pounds of pure crystallised sulphate of soda.

We give, also, below analysis of sulphate of soda from lakes controlled by Col. S. W. Downey, of Laramie. Of these deposits we know but little other than that they are situated about twenty-five miles south-west of Laramie, and, as indicated by the analyses, are contaminated by lime and magnesia salts to a considerable degree. Both analyses were made on samples previously calcined.

| | S. W. Downey's Wilcox Lake. | S. W. Downey's Red Soda. |
|---|---|---|
| $Na_2SO_4$ .. .. .. .. | 43·12 | 69·55 |
| $MgSO_4$ .. .. .. .. | 41·70 | 6·75 |
| $CaSO_4$ .. .. .. .. | — | 11·24 |
| NaCl . .. .. .. | 0·20 | 1·01 |
| Ignition .. .. .. | 0·32 | 0·33 |
| Insoluble.. .. .. | 16·15 | 10·50 |
| | 101·49 | 99·38 |

From a commercial standpoint these Wyoming deposits are interesting, inasmuch as they furnish cheaply and in large quantities quite a pure grade of sulphate of soda. This sulphate being free from iron, and also, of course, from free acid, is well adapted to use in the manufacture of glass. Freight rates from the East are in its favour, and allow a price that should yield a fair profit. Attempts have been made at Laramie on quite an elaborate scale, to manufacture soda-ash and caustic by the Leblanc process. These efforts were not remunerative.

## THE EFFECT OF DECOMPOSING ORGANIC MATTER ON NATURAL PHOSPHATES.

By Dr. N. T. LUPTON.

During the past two years especial attention has been called to the fertilising value of natural or raw phosphates, when applied alone in the form of floats and when mixed with organic matter, such as cotton-seed and cotton-seed meal.

If floats can be shown to produce as good results as acidulated phosphates, which is claimed by some, the cost of commercial fertilisers ought to be greatly reduced, and the extensive deposits of soft aluminous phosphates found in Florida and elsewhere find a ready sale. While the results of experiments are somewhat conflicting, there appear to be conditions under which floats, or ground raw phosphates, do produce as good, if not better, results than acid phosphates. The presence of decomposing organic matter is generally regarded as one of these conditions, but chemists are not agreed as to the precise nature of its action.

Liebig, in his letters on "Modern Agriculture," published in 1859, advances the theory that organic matter undergoing decay accumulates carbonic acid in the soil, and when rain falls it dissolves the carbonic acid, and thereby acquires the power of taking up phosphate of lime. This carbonic acid water does not withdraw from the soil the phosphate of lime contained in it, but wherever it meets with the granules of apatite or phosphorite, it dissolves a certain portion. Under these circumstances a solution of phosphate of lime must consequently be formed, which spreads in all directions around each granule. Wherever this solution comes in contact with soil not already saturated with phosphate of lime, the soil will take up and retain a certain portion of this salt. The portion of soil now saturated with phosphate will oppose no further obstacle to the wider diffusion of the solution.

Voelcker (*Bied. Centr.*, 1880, 866, 867), as quoted in the *Journal of the Chemical Society*, xxiv., Second Series, p. 640, draws the following conclusions:—

1. Phosphates are not readily taken up by plants in a soluble form, but must be returned to an insoluble condition before they yield their useful properties.

2. The efficacy of insoluble calcium phosphate corresponds with the minuteness of division in which it is found in a fertiliser.

3. The finer the particles in a phosphatic material, the more energetic its action as a manure.

Fleischer and Kissling (*Bied. Centr.*, 1883, 155, 161), on the application of insoluble phosphates to soils, found that the action of moorland soils when mixed with insoluble phosphates is to render a portion of the phosphate soluble in water, amounting to 5·5 per cent in one case of the total phosphoric acid; a portion at the same time was reduced to the di-calcium salt, and in one compost heap as much as 17 per cent of the total acid was brought into this form.

The general outcome of their experiments is that it is more advantageous to apply insoluble phosphate than superphosphate on humous soils, as they are capable of bringing insoluble phosphate into a soluble condition. This applies, however, only to peaty soils, as the presence of lime hinders this action.

In the *Journ. Chem. Soc.*, xxx., p. 774, is an abstract of an article from the *Journal of the Royal Agricultural Society*, 1884, by Dyer, which states that the first experiments made in 1882 in a stiff clay soil containing no calcium carbonate, ground and unground coprolites were used. The comparison was made with swedes both with and without manure; in each case the better result was from the undissolved phosphate. On the same plots, the following year, oats were grown without further addition of manure, and the produce was again, on an average, better where the undissolved phosphate had been employed. The following year 225 bushels of lime per acre were ploughed in before sowing. The same quantities of manure were applied as before. The season was dry and the crop small, but in this case the produce was better where the dissolved phosphate had been used. The ground coprolite contained more than twice as much phosphoric acid as the superphosphate.

Coming nearer home we find that experiments made at the Alabama Agricultural Station are of similar import.

In *Bulletin* No. 22, new series, January, 1891, we find the following statement:—"In several experiments previously conducted to ascertain the comparative agricultural value of the phosphate rock ground to impalpable powder, known as floats, with that of acidulated phosphate, the results have indicated that, used in conjunction with cotton-seed meal, floats are more profitable than the acid phosphate, taking into consideration the fact that floats contain nearly twice the percentage of phosphoric acid.

The soil used in these experiments was sandy drift that had been lying out many years. No commercial fertiliser had been previously applied to it."

To test more thoroughly the comparative productiveness of ground raw phosphate and acid phosphate under different conditions, and to determine whether decomposing organic matter converts insoluble into soluble phosphate, two sets of experiments were carried out, one on the farm and the other in the chemical laboratory, the results of which will now be given.

The materials used were carefully analysed by Dr. Anderson, assistant chemist, with the following results:—

The acid phosphate used gave—

| | | |
|---|---|---|
| Water-soluble phosphoric acid ($P_2O_5$) .. | 9·10 | per cent. |
| Citrate-soluble " " " .. | 2·94 | " |
| Acid-soluble " " " .. | 2·32 | " |
| Total phosphoric acid ($P_2O_5$) .. .. | 14·36 | " |

The Florida phosphate reduced to a fine powder, similar to floats, gave—

| | |
|---|---|
| Moisture .. .. .. .. .. .. .. | 4·18 |
| Insoluble matter.. .. .. .. .. .. | 32·39 |
| Total phosphoric acid (*acid-soluble*) | 16·54 |
| Iron and aluminium oxides .. .. | 8·89 |

None of the lime phosphate was soluble in water, and only 0·32 was soluble in ammonium citrate. The analysis shows an inferior grade of raw phosphate. The material purchased as "South Carolina floats" contained 2·26 per cent of available phosphoric acid in the form of citrate-soluble acid, and a total phosphoric acid of 28·73 per cent. The available phosphoric acid in each of the materials used in the experiments may be stated as follows:—

| | | |
|---|---|---|
| 1. Cotton-seed meal, available acid ($P_2O_5$) | 3·19 | per cent. |
| 2. Cotton-seed, " " | 1·03 | " |
| 3. Florida raw phosphate, " " | 0·32 | " |
| 4. South Carolina floats, " " | 2·26 | " |
| 5. Acid phosphate, " " | 12·04 | " |

Two qualities of land were selected at the station for the field experiments, one a strong red soil, the other a poor sandy soil. The results obtained were as follows; on the poor soil the fertilisers were sown broadcast:—

| | | Lbs. seed cotton per acre. |
|---|---|---|
| No. 1. | 400 lbs. pulverised Florida phosphate .. | 290·5 |
| " 2. | 800 " " " " .. | 219·8 |
| " 3. | 400 " acid phosphate .. .. .. .. | 196·7 |
| " 4. | 800 " " .. .. .. .. | 144·2 |
| " 5. | No fertiliser .. .. .. .. .. .. .. | 106·4 |
| " 6. | 400 lbs. Florida phosphate with 400 lbs. cotton-seed meal .. .. .. .. .. .. | 249·2 |
| " 7. | 800 lbs. Florida phosphate with 800 lbs. cotton-seed meal .. .. .. .. .. .. | 322·7 |
| " 8. | 400 lbs. acid phosphate with 400 lbs. cotton-seed meal .. .. .. .. .. .. | 252·0 |
| " 9. | 800 lbs. acid phosphate with 800 lbs. cotton-seed meal .. .. .. .. .. .. | 320·6 |
| " 10. | No fertiliser .. .. .. .. .. .. .. | 233·8 |

Each plot was one-seventh of an acre, and the usual precautions were taken to remove disturbing elements and have the conditions of cultivation and growth as uniform as possible. The details of the work were under the immediate supervision of Mr. Clayton, assistant agriculturist. On the strong red soil the fertilisers were applied in the drill with results as follows:—

| | | Lbs. seed cotton per acre. |
|---|---|---|
| No. 1. | 200 lbs. Florida phosphate with 200 lbs. cotton-seed meal.. .. .. .. .. .. | 1016·6 |
| " 2. | 400 lbs. Florida phosphate with 400 lbs. cotton-seed meal.. .. .. .. .. .. | 1105·6 |
| " 3. | 200 lbs. acid phosphate with 200 lbs. cotton-seed meal.. .. .. .. .. .. | 844·8 |
| " 4. | 400 lbs. acid phosphate with 400 lbs. cotton-seed meal.. .. .. .. .. .. | 1108·8 |
| " 5. | No fertiliser .. .. .. .. .. .. .. | 863·2 |
| " 6. | 200 lbs. Florida phosphate with 400 lbs. cotton-seed .. .. .. .. .. .. .. | 919·2 |
| " 7. | 400 lbs. Florida phosphate with 800 lbs. cotton-seed .. .. .. .. .. .. .. | 1182·4 |
| " 8. | 200 lbs. acid phosphate with 400 lbs. cotton-seed .. .. .. .. .. .. .. | 1178·4 |
| " 9. | 400 lbs. acid phosphate with 800 lbs. cotton-seed .. .. .. .. .. .. .. | 1387·2 |
| " 10. | No fertiliser .. .. .. .. .. .. .. | 931·2 |
| " 11. | 400 lbs. Florida phosphate .. .. .. | 892·8 |
| " 12. | 400 lbs. acid phosphate .. .. .. .. | 975·2 |
| " 13. | 400 lbs. cotton-seed meal .. .. .. | 1271·2 |
| " 14. | 800 lbs. cotton-seed .. .. .. .. | 1294·4 |

The land was not uniform in natural productiveness, but improved in quality from the first to the last plot. While the results are not perfectly uniform the pulverised raw phosphate evidently produced as good, if not better, results than the acid phosphate, whether used alone or mixed with cotton-seed and cotton-seed meal.

Anticipating these results, experiments were carried on in the laboratory during the summer to determine whether they are due to the fact that decomposing organic matter converts insoluble or acid-soluble lime phosphate into the available or citrate-soluble condition. For this purpose half-gallon wide-mouthed glass jars were used, and the following mixtures placed in each:—

No. 1. 2 lbs. Florida phosphate with ½ lb. cotton-seed meal.

No. 2. 1 lb. Florida phosphate with ½ lb. cotton-seed meal.

No. 3. 2 lbs. South Carolina floats with ½ lb. cotton-seed meal.

No. 4. 1 lb. South Carolina floats with ½ lb. cotton-seed meal.

No. 5. 2 lbs. Florida phosphate with ½ lb. cotton-seed.

No. 6. 1 lb. Florida phosphate with ½ lb. cotton-seed.

No. 7. 2 lbs. South Carolina floats with ½ lb. cotton-seed.

No. 8. 1 lb. South Carolina floats with ½ lb. cotton-seed.

The contents of each jar were rubbed up in a porcelain mortar moistened with water, and mixed as thoroughly as possible. The mixtures were stirred frequently, in fact nearly every day. Fermentation began within a day or two, and continued during the whole period of the experiments. Samples for analysis, that is, for the determination of available phosphoric acid, were taken from the jars and analysed, with results as follows:—

| Date of taking sample. | Per cent of available $P_2O_5$ found. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. |
| July 2. | 0·99 | 1·69 | 2·68 | 3·04 | 0·58 | 0·54 | 2·77 | — |
| ,, 9. | 1·25 | 1·62 | 2·89 | 2·64 | 0·72 | 0·95 | 2·33 | 2·27 |
| ,, 16. | 1·25 | 1·61 | 2·89 | 2·82 | 0·72 | 0·80 | 2·29 | 2·26 |
| ,, 23. | 1·16 | 1·80 | 3·37 | 3·22 | 0·84 | 0·49 | 2·37 | 2·39 |
| ,, 30. | 1·12 | 1·60 | 3·02 | 3·38 | 0·72 | 0·53 | 1·81 | 2·70 |
| Aug. 6. | 1·41 | 1·79 | 2·87 | 3·15 | 0·82 | 1·08 | 2·49 | 2·57 |
| ,, 20. | 1·41 | 1·57 | 2·73 | 3·26 | 0·81 | 1·00 | 2·15 | 2·53 |
| Sept. 3. | 1·50 | 2·16 | 2·75 | 3·27 | 1·16 | 1·10 | 1·96 | 2·51 |
| ,, 17. | 1·41 | 1·75 | 2·56 | 2·91 | 1·07 | 0·89 | 2·04 | 2·32 |
| Oct. 1. | — | 2·28 | 2·97 | 3·14 | 0·99 | 1·26 | 2·57 | 2·51 |

The above results seem to show that the fermentation of the cotton-seed and cotton-seed meal had very little, if any, effect on the Florida ground phosphate or the South Carolina floats in converting the insoluble into soluble phosphate. The slight variation in the results, though favouring to some extent the conclusion that there is a slight increase in the available phosphoric acid, may be accounted for on the ground of personal error or the want of uniformity in the mixing of the materials, since it is difficult, if not impossible, to secure perfect uniformity in a mixture of ground phosphate and cotton-seed.—*Journ. Amer. Chem. Soc.*, xiv., No. 10.

# NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

## Part I.—*General Remarks.*

All petrologists who have worked much with the microscope must have felt the want of a system of micro-chemical analysis at once simple and reliable. Having devoted some time to the study of micro-chemical reactions, I think it may save the time and labour of students who propose to take up the subject if I give them the result of the experience I have gained up to date.

In order to shorten this paper as far as possible, I have limited myself to the bases that commonly enter into the composition of rock-making minerals, and have excluded those which relate to ores.

Micro-chemical analysis is not only an essential adjunct to micro-petrological research, but it is capable of rendering some aid to the ordinary chemist. Not only does it afford a ready means of testing precipitates, but it is even more essential as a method for testing the purity of reagents.

Until I took up this inquiry I had no idea of the *extent* to which the reagents supplied by some good firms contain chemical impurities. I was astonished to find, for instance, that my bichloride of platinum invariably showed the presence of potash in every mineral I tested with it; that my fluosilicic acid always indicated the existence of an appreciable amount of soda; and my aluminium sulphate, delusively labelled "purified," contained so much potash that it crystallised on my glass slides as an alum. I mention these cases as mere illustrations. I have succeeded in obtaining some chemicals sufficiently pure to work with; but in other cases I have failed to do so. Pure uranium acetate, for instance, is said to belong to the rhombic system, and to crystallise in long prisms; but though I have had uranium acetate specially made for me, all that I have obtained crystallises in the cubic system in forms identical with those of the double salt of acetate of sodium and uranium. As a test for soda, therefore, by the microscopic method, it is worse than useless.

In micro-chemical analysis I have found the following system the most convenient to pursue. I convert the bases present in the minerals under examination into sulphates,† and, with one or two exceptions to be noted further on, work with these sulphates in aqueous solution without the aid of heat. There is considerable advantage, it seems to me, in working with salts in the form of sulphates; most of them are soluble in water; they are all insoluble in absolute alcohol, and Canada balsam diluted with benzole or chloroform does not corrode them. Scarcely any of those entered in Part II. are deliquescent; whilst the alums are the only ones that crystallise in the cubic system.

All the sulphates can be mounted in Canada balsam with the greatest ease, and preserved for any number of years for future study. The microscopist therefore can dispense with the aid of figured illustrations; he can form, what is far better, an imperishable collection of typical specimens of the salts themselves to be always at hand for ready reference.

Other salts besides the sulphates can be mounted in Canada balsam, but the mounting and preservation of some of them are extremely difficult. Many of the chlorides, for instance, deliquesce, rendering the use of heat in some form necessary; many are corroded by Canada balsam; and many crystallise in the cubic system, rendering their identification more difficult. Potassium chloride, for instance, cannot be distinguished from sodium chloride under the microscope.

Having obtained a solution of a sulphate, or a mixture of sulphates, I place a drop of the solution on a glass slide and allow it to evaporate spontaneously in a place free from wind, draught, or dust. I find a shelf in a glass book-case a suitable place. Five or six slides should be prepared at the same time. The next day two or three of the most perfect of these should be selected for mounting, but it is material to preserve an unmounted specimen for subsequent comparison with the mounted

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* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

† Silicates, insoluble in sulphuric but soluble in hydrofluoric acid, I convert into sulphates by dissolving them in a state of fine powder in hydrofluoric acid, in a platinum vessel, with the aid of heat. I then add sufficient sulphuric acid to convert the bases into sulphates. On evaporation to dryness the silica is driven off in the form of fluosilicic acid, and the sulphates are left behind. These can now be dissolved in water, or, in the case of barium or strontium, in hot sulphuric acid. A similar process can be used to test the purity of the hydrofluoric acid employed, viz., add concentrated sulphuric acid to the HF aq. and evaporate to dryness. If the HF contains bases in any appreciable quantity they will be left behind as sulphates, and may be detected under the microscope. In the case of minerals not soluble in hydrofluoric acid they must be decomposed by fusion with carbonate of soda or some other flux. See *Zircon*, Part III.

ones. The unmounted slide enables us to observe whether the salt effloresces, deliquesces, becomes opalescent, or has a silky lustre. Information regarding its refraction can also be obtained, for salts, like gypsum, whose index of refraction is very close to that of balsam, will, when mounted in th atmedium become invisible, or nearly so, in ordinary transmitted light.

The material I use for mounting is Canada balsam diluted with chloroform until it flows freely. I keep it in a small stoppered bottle, and find one of about ½ an oz. capacity very convenient. I pour this balsam very carefully, drop by drop, on the crystals to be mounted, place a thin cover-glass over the balsam, and allow the latter to consolidate by the spontaneous evaporation of the chloroform without subjecting the preparation to pressure or heat. From one to three days is sufficient, in ordinary cases, for the consolidation of the balsam.

I have found it convenient to divide this paper into three parts. The present part (Part I.) is devoted to remarks of an explanatory character. Part II. contains, in a tabular form, a list of sulphates with the most important or best known of their hydrates and double salts. It contains chemical information gleaned from various standard works on chemsstry. The optical system to which each salt belongs, and its chemical formula, are given in Cols. 1 and 4 on the authority of either Fock (*Krystaltographisch-Chemische Tabellen*, 1890) or Roscoe and Schorlemmer ("A Treatise on Chemistry," vol. ii. The Metals. New Edn.). Col. 5 indicates the form in which the salt appears when crystallised on a glass slide by the method above described, and embodies in every case the result of my own observations.

The forms described in col. 5 will not be found to agree, in every case, with the crystals figured in mineralogical or ordinary chemical works. The crystals figured in such works are often natural minerals formed in the laboratory of Nature under conditions that cannot be reproduced by the micro-chemical student; in other cases they are typical examples of exceptionally perfect crystals selected from a large number obtained by the crystallisation of a considerable quantity of material from saturated solutions. For our purposes we must be content with the results that can be obtained by allowing a drop of an aqueous solution to crystallise on a glass slide by spontaneous evaporation. The conditions under which crystallisation takes place in the latter case differ from those which obtain in the cases above referred to, and the results are therefore sometimes considerably modified. The material at the disposal of the microscopist is often extremely small, and his methods, to be of any value, must be capable of dealing with small quantities.

Cols. 6, 7, and 8 contain optical observations for which I am responsible. Cols. 6 and 7 require a few words of explanation. I have given the order of colours exhibited by the crystals according to Newton's scale,* as I think this affords a rough mode of determining the double refraction of these salts which is of some practical value. Colours, no doubt, depend not only on the strength of the double refraction, and the direction taken by the light in its passage through a crystal, but also on the thickness of the crystal. But in dealing with the results of the spontaneous evaporation of an aqueous solution on a glass slide, I think it will be generally found that each salt has a habit of its own in respect of the general size and general thickness of its crystals as well as of the faces on which they commonly lie, and that therefore they will generally yield fairly similar results as regards colours in polarised light. It will be found that whilst certain salts habitually yield colours as high as the 7th order, others never give colours higher than those of the 1st, 2nd, or 3rd order, as the case may be. By discarding from consideration specially thin and attenuated crystals deposited when nearly the whole of the material in the drop had been exhausted, and by selecting for observation the crystals that exhibit the strongest double refraction, we obtain data of some value. Treated in this way the colours afford a rough practical guide to aid us in determining the identity of the salt. The order of colour recorded in Col. 6 is the maximum observed by me.

In Col. 7 the direction of the major axis of elasticity has been determined with the aid of the quartz wedge. When it is said to be "‖ to *e*" it is intended to imply that when the axis of the quartz wedge is parallel to the axis of elongation of the crystal the phenomenon of *thinning* is produced. I have employed (*e*)* as an abbreviation for the ordinary direction of elongation because it excludes any pretence of absolute precision. Some salts habitually lie on one face on the glass slide and are elongated in one direction. In practice I find the direction of the major axis, as indicated in Col. 7, an aid to the determination of salts of great practical value.

In Col. 8 I have alluded to a phenomenon observed when the polariser is used without the analyser which is usually attributed to "absorption." Calcite, and some other colourless minerals, when examined in transmitted light with the polariser alone, exhibit dark lines, shadows, and dark markings, in a certain position of the polariser (or when the polariser is rapidly revolved) which disappear altogether when the plane of vibration of the nicol is altered relatively to the plane of vibration of the light passing through the mineral. Some salts possess this property in a high degree—others in a much less degree or not at all. When a colourless salt, or mineral, possesses this absorption conspicuously, it marks it off from other minerals that do not display the property. We have here therefore a mode of distinguishing colourless minerals from one another which I have endeavoured to utilise in Col. 8.

(To be continued.)

## NOTICES OF BOOKS.

*Foundations of the Atomic Theory*: comprising Papers and Extracts. By John Dalton, William Hyde Wollaston, M.D., and Thomas Thomson, M.D. (1802—1808). Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co. 1893.

This publication is the second of the interesting series known as the "Alembic Club Reprints." It comprises John Dalton's "Experimental Enquiry into the Proportion of the several Gases or Elastic Fluids constituting the Atmosphere." This memoir was originally read on November 12th, 1802, before the Literary and Philosophical Society of Manchester, and may be found in the second series of their *Transactions* (vol. i., 1805, pp, 244—258). It is of capital importance as presenting the first definite example of the law of multiple importance.

A second paper, read also by Dalton on October 21st, 1803, treats of the absorption of gases by water and other liquids, and includes the author's earliest Table of Atomic Weights. Here hydrogen is taken as =1.

Two short papers follow from Dalton's "New System ef Chemical Philosophy,"—"On the Constitution of Bodies" (pp. 141—143), and on "Chemical Synthesis" (pp. 211—216 and 219—220). Here the author seems to adopt the view that analysis and synthesis go no farther than to the separation of particles, one from another, and to their reunion. Dalton's system of chemical symbols is also included.

A paper on Super-acid and Sub-acid Salts, by W. H. Wollaston, M.D., next follows. It was originally read before the Royal Society, Jan. 28th, 1808, and may be found in the *Phil. Trans.* (vol. xcviii., 1808, pp. 96—102).

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* For the mode of ascertaining the order see my paper on Double Refraction of Minerals, *Geol. Mag.*, 1888, p. 548. Also p. 65 of "Rosenbusch's Microscopical Physiography," by Iddings.

* I have occasionally given *c* when the vertical crystallographic axis is intended.

Here we find a fore-shadowing of stereo-chemistry. The author thinks that we shall be obliged to acquire a geometrical conception of their (the atoms) relative arrangement ln all the three dimensions of solid extension.

Lastly, come extracts from a paper on Oxalic Acid, by Dr. Thomas Thomson, F.R.S.E., and inserted in the *Phil. Trans.* (vol. xcviii., 1808, p. 63). This brief paper is an appreciative notice of Dalton's atomic theory.

We think that our brief remarks may draw attention to these fundamental documents of chemistry, especially as they are not universally accessible in their original forms.

## CORRESPONDENCE.

### THE CHICAGO EXHIBITION.

*To the Editor of the Chemical News.*

Sir,—I send you manuscript of an invitation to be issued especially to English speaking chemists, inviting them to take part in the Chemical Congress of the World's Auxiliary of the World's Columbian Exposition, to be held in Chicago in August next.

Special invitations have been sent to nearly all prominent English chemists, but it is believed that the publication of the enclosed circular in the Chemical News will reach a number of chemists who otherwise would fail to get an invitation.—I am, &c.,

H. W. Wiley,
Chief of the Chemical Division,
and Chairman of the
General Committee on
World's Chemical Congress.

U.S. Dept. of Agriculture,
Division of Chemistry,
Washington, D.C.,
June 24, 1893.

The World's Congress Auxiliary of the World's Columbian Exposition.
Department of Science and Philosophy.
General Division of Chemistry.

The Committees in charge of the Congress have selected Monday, August 21st, as the date of the opening of the Congress of Chemistry to be held in connection with the Columbian Exposition in Chicago.

The chairman of the committee appointed for cooperation in this Congress by the American Association for the Advancement of Science, Chemical Section, is Prof. Ira Remsen, Johns Hopkins University, Baltimore, Md. The chairman of the committee appointed by the American Chemical Society is Dr. Wm. McMurtrie, 106, Wall Street, New York, N.Y. The chairman of committee of the World's Congress Auxiliary, on Congress of Chemists, is Prof. John H. Long, 2421, Dearborn Street, Chicago, Ill. The various committees have organised by selecting Dr. H. W. Wiley, Chief Chemist of the Department of Agriculture, Washington, D.C., as Chairman, and Prof. R. B. Warder, Howard University, Washington, D.C., as Secretary.

The work of the Congress has been divided into ten sections and a temporary chairman has been selected for each section, as follows:—

Agricultural Chemistry—H. W. Wiley, Department of Agriculture, Washington, D.C.
Analytical Chemistry—A. B. Prescott, Michigan University, Ann Arbor, Mich.
Didactic Chemistry—W. E. Stone, Lafayette, Ind.
Historical Chemistry and Bibliography—H. Carrington Bolton, University Club, New York.
Inorganic Chemistry—F. W. Clarke, Geological Survey, Washington, D.C.
Organic Chemistry—I. Remsen, Johns Hopkins University, Baltimore, Md.
Physical Chemistry—R. B. Warder, Howard University, Washington, D.C.
Physiological Chemistry—V. C. Vaughan, Michigan University, Ann Arbor, Mich.
Sanitary Chemistry—H. Leffmann, 715, Walnut Street, Philadelphia, Pa.
Technical Chemistry—Wm. McMurtrie, 106, Wall Street, New York, N.Y.

General and special invitations have already been issued to foreign chemists and many replies have been received, indicating a large attendance of chemists from abroad at the Congress.

The following distinguished foreign chemists have already promised to present papers to the Congress, and the list will without doubt be increased many fold before the date of the opening:—

Prof. L. G. Ernest Miliau, Marseilles—On Standard Methods of Oil Analysis.
Mr. Farnham Maxwell Lyte, London—On the Production of Chlorine.
Mr. H. Droop Richmond, London—On the Accuracy of the Methods of Analysis of Dairy Products.
M. Pierre Manhes, Lyon—Subject to be announced later.
Prof. B. Tollens, Göttingen—Researches on the Synthesis of Polyatomic Alcohols.
Prof. Ferd. Tiemann, Berlin—Subject to be announced later.
M. H. Pellet, Brussels—On the Methods of Determining the Percentage of Sugar in Beets.
Mr. H. R. Procter, Leeds—On the Examination of Tanning Materials.
M. O. Kemna, Antwerp—On the Purification of Water.
Mr. Otto Hehner, London—Subject to be announced.
Prof. C. A. Bischoff, Riga—Subject to be announced.
Prof. G. Lunge, Zürich—On the Method of Teaching Technological Chemistry at Universities and Polytechnic Schools.
Prof. Ludwig Mond, Rome—Subject to be announced.
Prof. W. N. Hartley, Dublin—Subject to be announced.

This circular is specially intended to reach American chemists, inviting them to take an active interest in the Congress, and to be present; or, if that is not possible, to send papers on some of the subjects indicated in the classification above mentioned.

Chemists specially interested in each of the subjects for discussion are invited to correspond with the chairmen of those sections in regard to the character of the work and of the papers expected. All chemists who expect to read papers at the Congress are earnestly requested to send the titles thereof to the Chairman of the General Committee, Dr. H. W. Wiley, Department of Agriculture, Washington, D.C., on or before the 1st day of August. It will be difficult to arrange for a position on the programme for the titles of any papers which may be received after that date. The time required for each paper should also be noted so that daily programmes can be provided for in advance. In all cases the place of honour on the programme will be given to foreign contributors. Papers or Addresses can be presented in English, French, or German, as the author may select; but where convenient, the English language will be preferred.

The Committee desires to ask those chemists who propose to attend the World's Congress to make an excursion, during the week previous to the meeting, to Madison, Wisconsin, for the purpose of attending the meetings of the Chemical Section of the American Association for the Advancement of Science. This will not only be a delightful excursion, as Madison is distant only about four hours from Chicago, but will also enable the participants in the Congress to make the acquaintance of the scientific men of the United States and other countries engaged, not only in chemical, but also in other branches of science.

Other attractions in Chicago will be meetings of different Chemical Societies. Among these may be mentioned the American Chemical Society, the Annual

Meeting of which will begin August 21st, and the Association of Official Agricultural Chemists, which will hold its Annual Meeting in Chicago, beginning Thursday, August 24th. The Sessions of these Societies will be so ordered as not to conflict with the business of the Congress. The American Pharmaceutical Association, which has a strong Chemical Section, will also meet in Chicago at or near this time. It is hoped that the Institute of Mining Engineers may also hold its meeting about this time, although no definite announcement can be made in regard to this matter. It is thus seen that this occasion will bring together the active workers in all branches of chemical science in the United States, and enable American chemists to make the acquaintance of distinguished co-labourers from abroad, and the visiting chemists to meet the largest possible number of their fellow labourers here.

Every possible arrangement will be made for the convenience and comfort of visitors. Intending participants in the Congress should address Prof. John H. Long, 2421, Dearborn Street, Chicago, Ill., for information in regard to quarters and other accommodations. On arrival in Chicago, visitors should report at once to the Congress Headquarters, Art Institute Building, Lake Front and Adams Street, where full information will be given them in regard to matters connected with their personal comfort. Wherever possible, intending visitors should write a few days before their arrival to the Committees above-mentioned, in order that special provision may be made for their comfort when they reach Chicago.

In regard to the climate of Chicago in August much can be said in praise. While warm days may sometimes be expected, the situation of the city on the edge of a vast open prairie extending for nearly a thousand miles north and west without a break, secures, even in the hottest day, refreshing breezes which cool the atmosphere and mitigate the heat of summer. The lake breezes also do much to render the climate moderate. No one need be deterred from attending the Congress on account of fear of severe heat.

It is especially urged that all chemists who intend visiting the World's Fair take this occasion to do so, by which they can combine the pleasure of visiting the Exposition with the benefit derived from attendance at the Congress. To American chemists an especial appeal is made to be present for the purpose of welcoming our foreign visitors, and showing them the progress of Chemical Science in the United States.

Harvey W. Wiley.

## THE ORGANISATION OF SCIENCE.

*To the Editor of the Chemical News.*

Sir,—Mr. Swinburn's letter in *Nature* of June 29, is one more piece of evidence to show that workers in the various branches of Science are at last waking up to a realisation of the necessity of replacing the present happy-go-lucky machinery of science by a thorough re-organisation—a necessity which I pointed out at some length in my pamphlet on the "Organisation of Science" over a year ago. Since that pamphlet appeared, we have had long letters from zoologists, geologists, and now from a physicist, all groaning at the waste and inefficiency involved in the present unsystem, and supporting, to a large extent, practically the same reforms as those suggested in my pamphlet.

To comment upon Mr. Swinburne's letter at the length which the subject deserves, would be to make an unreasonable demand upon your space; and there is the less necessity for this, since most of his difficulties are answered by anticipation in my pamphlet; but perhaps you will permit me a few words in reply to him.

If Mr. Swinburne will refer to pp. 19—23 of my essay, he will find a scheme worked out by which a *decentralisation* of scientific meetings (that is to say, a provision for meetings in the provinces and not in London only) would be secured, together with a complete *centralisation* of the publishing—in effect a federation of all the societies concerned in any *one* branch of science; and a splitting up of all societies and journals of proceedings, concerned with half a dozen different subjects.

With regard to the Royal Society, which I am relieved to find myself not alone in considering a stumbling-block to scientific organisation in the present day, I have already pointed out a simple remedy, viz., that it should refuse to receive any papers that come within the scope of the various specialist sciences, and should, instead, co-ordinate and collate the work of all the sub-societies (pp. 6—14).

I am sorry that Mr. Swinburne has seen fit to adopt the specialised tone of a simple physicist, since the evil is common to *all* branches of science, and reform is necessary for Physics no more than for the rest of science; but I am still more sorry he has seen fit to put forward the *dignity* of the Physical Society as a hypothetical obstacle to reform. I must emphatically protest against the notion that the Physical or any other society has any single interest to consult other than how best to subserve that science which it was founded to minister unto. The only true *dignity* of any such society consists in loyally ministering to the wants of science, and in a complete readiness to, at any time, *even efface itself*, if such proceeding be advantageous to science. Therein lies the whole duty and dignity of the Physical, as of every other society; and any suggestion contary to this cometh of evil. The Physical Society exists for the advancement of Physics; not Physics for the promotion of the Physical Society's dignity.—I am, &c.,

A Free Lance.

London, June 30, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 25, June 19, 1893.

**Extraction of Zirconia and Thoria.**—L. Troost.—This paper will be inserted in full.

**Study of certain Novel Phenomena of Fusion and Volatilisation produced by the Heat of the Electric Arc.**—Henri Moissan.—This memoir requires full insertion.

**Study on the Filtration of Liquids.**—R. Lezé.—The author's method is to submit the liquid in question to very rapid rotation in a porous vessel. The speed of efflux of distilled water being taken as unity, the following values were found for:—

| | | Rate of efflux. |
|---|---|---|
| NaCl .. .. .. .. | 5 per cent | 1·023 |
| KCl .. .. .. .. | 5 " | 1·043 |
| Sodium nitrate .. .. | 5 " | 1·051 |
| Ammonium sulphate.. | 5 " | 0·993 |
| Alcohol at 20° .. .. | | 0·590 |
| " " 40° .. .. | | 0·50 |
| " " 90° .. .. | | 0·67 |
| Milk .. .. .. .. | | 0·03 |
| Sewage .. .. .. | | 0·10 |

**Combinations of Molybdates and Sulphurous Acid.**—E. Péchard.—It results from the facts stated that sulphurous acid does not act upon alkaline molybdates in the manner of ordinary reducing agents, the difference depending on the formation of molybdosulphites. Reduction occurs only if the liquid is strongly acid. Selenious acid yields with the molybdates analogous compounds, but much more stable.

**On the Bromoboracites. Iron and Zinc Bromoboracites.**—G. Rousseau and H. Allaire.—The composition of iron bromoborate is shown by the formula $6FeO,8B_2O_3,FeBr_2$. It always contains a small quantity of lime, which replaces, isomorphically, an equivalent proportion of ferrous oxide. It appears as a greyish white powder, consisting of a mixture of cubes and tetrahedra, acting upon polarised light like natural boracite. The zinc compound, $6ZnO,8B_2O_3,ZnBr_2$, forms white microscopic crystals of a pseudocubic symmetry, acting upon polarised light.

**Copper Fluorides.**—M. Poulenc.—The hydrated fluoride, $CuFl_2 2H_2O$, has been already obtained by Balbiano. The author has succeeded in obtaining the cuprous fluoride $Cu_2Fl_2$ in the anhydrous state by the action of gaseous hydrofluoric acid upon cuprous chloride. When fused it appears as a transparent mass, of a ruby-red colour, and of a crystalline fracture. Cupric fluoride, $CuFl_2$, is obtained by the action of melted ammonium fluoride upon hydrated cupric fluoride. It is a white crystalline powder, which gradually turns blue on exposure to the air.

**Action of Electricity upon the Carbidation of Iron by Cementation.**—Jules Garnier.—At about 1000°, under the action of a very weak current (50 ampères and 2·5 volts) the conversion of iron into steel takes place with great rapidity.

**Rotatory Power of Bodies belonging to a Homologous Series.**—Ph. A. Guye.—This paper does not admit of abstraction.

**Rotatory Power of the Ethers of Valerianic and Glyceric Acid.**—Ph. A. Guye and L. Chavanne.—This paper also is not adapted for abstraction.

**Formation-heat of certain Derivatives of Indigo.**—R. d'Aladern.—The formation-heat of indigotine is given as +41·0 cal.; that of isatine = +59·0 cal.; that of sathyde is +145·0; and that of dioxyindol +80·2 cal.

**On Dextro-licareol.**—Ph. Barbier.—Licareol exists in two modifications, dextro-rotatory and lævo-rotatory.

**New Apparatus for Measuring the Intensity of Perfumes.**—Eugene Masnard.—The author proposes the use of a general method and a new apparatus for determining the intensity and persistence of perfumes, founded on the property of oil of turpentine to prevent the luminosity of phosphorus in darkness.

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*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 11.

**A Study on the Rate of Decomposition of the Diazo-Compounds.**—J. Hausser and P. Th. Müller.—The authors have examined the diazotoluene sulphate and the diazobenzenecarboxylated sulphates. The para-compounds are the most stable, the meta-compounds the least stable, whilst the ortho-compounds take an intermediate position.

**The Odoriferous Power in the Fatty Series.**—Jacques Passy.—Already inserted.

**Action of Acetic Acid and of Formic Acid upon Turpentine.**—MM. Bouchardat and Oliviero.—The action of formic acid upon turpentine in presence of water is distinguished by its violence, destroying the rotatory power, and by the abundant formation of free terpine, which, with acetic acid, is observed only to a very slight extent.

**Convenient and Expeditious Process for Saponifying the Nitriles.**—L. Bouveault.—This paper is not adapted for useful abstraction.

**Preparation of Triphenylacetonitrile and Triphenylcarbinol.**—L. Bouveault.—The author prepares triphenylcarbinol by decomposing triphenylbromomethane with water. Triphenylbromomethane is best obtained by the process of Allen and Kölliker, which consists in letting the calculated quantity of bromine fall drop by drop upon melted triphenylmethane heated to 130°.

**Hydrazone of Cyanacetone.**—L. Bouveault.—A critique of the process of Mr. Burns (*Journ. Prak. Chemie*).

**Pyruvic Ether and its Product of Condensation in Presence of Hydrochloric Acid.**—P. Genviesse.—The author has obtained pure pyruvic ether, and studied its action upon gaseous ammonia. He has obtained for the first time methyl-2-pentene-2-one-4-dioïc acid, prepared its copper and silver salts and its ethylic ether, and shows that pyruvic ether behaves like acetylacetic ether with hydrochloric acid.

**Oxyhæmatine, Reduced Hæmatine, and Hemochromogen.**—H. Bertin-Sans and J. Moitessier.—The direct action of reducing agents upon alkaline solutions of oxyhæmatine produces not hemochromogen, but a compound not as yet described, which we shall call reduced hæmatine, and which is characterised by a special spectrum. Pure oxyhæmatine, prepared by Cazeneuve's process and dissolved in soda at 1 per cent, presents an absorption-spectrum consisting of a single band with blunted margins, situate between C and D, the middle of which coincides with $\lambda = 618$. The addition of a reducing salt, such as neutral potassium sulphide, causes the rapid disappearance of this band and the appearance of an analogous band, the middle of which coincides with the ray D. The authors ascribe this spectrum to the formation of reduced hæmatine. If to reduced hæmatine we add a slight excess of ammonia or of an amine, the band of reduced hæmatine disappears, and the solution gives very distinctly the spectrum of hemochromogen.

**Action of Carbon Monoxide upon Reduced Hæmatine and Hemochromogen.**—H. Bertin-Sans and J. Moitessier.—The authors have obtained a compound of carbon monoxide with hematine by setting out directly from reduced hæmatine without the intervention of hemochromogen. Without absolutely asserting that the compound formed under these conditions differs decidedly from the compounds described by Popoff, Jaegerholm, and Hoppe-Seyler, it seems to present greater guarantees of purity.

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Errata.—Vol. lxvii., p. 313, col. 1, in every case, *for* "Olouchoff" *read* "Obouchoff." Line 31, *for* "Pfoltzer" *read* "Holtzer."

THE CHEMICAL NEWS.

Vol. LXVII., No. 1756.

## AN IMPROVED METHOD OF PURIFYING TOLUOL, BENZOL, &c.

By R. J. FRISWELL.

Of late years the demand for toluol has so much increased that large quantities of the by-products from the oil gas factories have been worked up to recover the toluol and benzol which Armstrong some years back discovered in them.

This has caused much trouble in separating traces of paraffins, which, though not so troublesome with benzol, render toluol almost unworkable, unless treated in a special manner. These substances are not indicated by any variation of the boiling-points which are now uniformly good, but can be at once detected by vigorously shaking the sample with an equal volume of pure sulphuric acid of 1·842 sp. gr.

Under these circumstances a sample made from pure coal oils separates sharply into two layers when allowed to rest after shaking, and the acid is colourless, or of a very faint brown tint, and so remains for twenty-four hours or more.

On the contrary, the samples contaminated with these bodies form an emulsion, which takes five to ten minutes to separate completely, and the acid is more or less bright orange-coloured. In about one hour the surface of the acid is deep green, and this tint gradually spreads through the liquid, so that in ten to twelve hours the whole is deep green, or even black, while a distinct odour of sulphurous acid is easily detected.

A sample of toluol behaving in this way may be at once rejected by anyone desiring to avoid an immense amount of trouble in working it.

It is, however, an easy matter to render toluol quite equal to the best samples prepared from pure coal oils by a very simple and inexpensive treatment.

It is, of course, well known that agitation with concentrated oil of vitriol will effect the removal, by solution, of most of these bodies; but unfortunately at the same time great loss of toluol occurs, owing to its easy solubility in the acid. Its recovery by hydrolysis is, needless to say, an expensive operation.

It is no secret that many makers have used fuming acid, and have alleged that, notwithstanding increased loss, it has proved cheaper to use than ordinary vitriol. The use of oxidising agents dissolved in the vitriol has been found quite ineffective.

The movement in the direction of stronger acid is an entirely erroneous one, and the secret of success lies in an opposite direction.

It is quite possible to employ an acid too weak to dissolve the toluol, but quite strong enough to wash out the paraffins; but this treatment is rendered expensive by reason of the large volume of acid and number of treatments required. It is, however, possible to make use of an acid which shall act in a different manner, viz., render the paraffin-like bodies, part of which it dissolves, much less volatile by polymerising them.

This may be carried out as follows:—Crude toluol boiling between 110°—130° C. is agitated thoroughly for four hours with 10 per cent by volume of sulphuric acid of sp. gr. 1·803. It is allowed to rest, and drawn off from the acid in the usual manner, and washed once with enough caustic soda to remove traces of acid. Very thorough agitation is necessary, and certain samples may require more acid or a longer time of treatment. The loss should not exceed 5 per cent.*

It is then at once transferred to the rectifying still, and the pure toluol taken off. This will be found by the acid test quite equal to the best toluol made from coal oils. In fact 95 per cent of the distillates will pass this test.

The residues in the still consist partly of the polymerised bodies, their boiling-points lying between 260° and 285° C.

The waste acid on dilution deposits a deep green oil, which, when nearly free from acid, is soluble in water. When distilled with water a very heavy oil comes over with the distillate. The acid cannot be recovered unless this substance is separated by dilution, as, if heated directly as drawn from the toluol, it evolves large volumes of sulphurous oxide and becomes nearly solid from separation of carbon.

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* About half of this is due to the paraffins removed.

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## THE AVAILABILITY OF THE FLUORESCEIN REACTION FOR THE DETECTION OF SACCHARINE IN BEER.

By F. GANNTER.

Börnstein has recommended in the *Zeit. für Analyt. Chemie* (xxvii., 167), as a very sensitive reaction for saccharine, the formation of fluorescein on heating saccharine with concentrated sulphuric acid and resorcin. The value of this reaction has been contested by Hooker (*Berichte*, xxi., 3395), since on treating resorcin alone with concentrated sulphuric acid, a reaction occurred apparently the same as that described by Börnstein as characteristic of benzoic sulphide.

Börnstein, in a reply, admitted that many organic compounds, on suitable treatment, yielded liquids with a greenish surface-reflection, but that these were all so far inferior in intensity to the fluorescence caused by sulphinide that the latter—on a proper management of the experiment—may serve very well for establishing the presence of saccharine. According to these enlargements, the reaction appeared not alone very sensitive; but, in comparison to the other methods, by conversion into a sulphate or salicylic acid, very simple and convenient. As I had to test a great number of samples of beer for saccharine, I was induced to study the reaction more closely.

In the first place, to test the behaviour of pure resorcin, a few grms. of it were heated with from 3 to 5 drops of concentrated sulphuric acid in the manner described by Börnstein. The solution became at first light red, then dark brown, and finally dark greenish black. After diluting with water and adding soda-lye until the reaction became alkaline, no change of colour was observed, the solution remained reddish brown, had on its surface scarcely a greenish reflection, and displayed certainly no fluorescence. In various other experiments repeated with the addition of various organic substances an unmistakable fluorescence was never observed. Ten m.grms. of a saccharine tablet (saccharine + sodium bicarbonate) was treated in exactly the same manner: the reaction ensued exactly as described by Börnstein. The solution became yellowish red, then deep green, and on dilution with water had a deep reddish brown colour, which on the addition of soda-lye displayed a distinct sharp change to dark green. On further dilution the liquid appeared yellowish red by transmitted light, but by reflected light intensely green fluorescent; which even on dilution to 1 and upwards retained this property. Repeated experiments with still smaller proportions of saccharine always gave the same very strong fluorescence, not to be mistaken even on great dilution.

The reaction can therefore without doubt serve for the recognition of the smallest quantities of saccharine.

Börnstein further mentions that the phenomenon of fluorescence in the reaction occurs only further in presence of phthalic anhydride and phthalimide; and I thence on the basis of the above experiments concluded that the reaction might be directly used for the detection of saccharine in beer. Therefore the beer was evaporated down, extracted with ether in the manner described below, and the reaction was effected with the residue left after the evaporation of the ether, which must contain any saccharine present. Twelve beers treated in this manner gave, without exception, a very intense fluorescence, so that on the faith of this reaction alone an addition of saccharine must have been assumed as beyond all doubt. But in each of these beers I had tested the ethereal residue with the tongue, and in eleven cases I had found a sharply burning strongly bitter taste, without any sweetness. One sample, however, gave at first an unmistakable sweetness, followed by a strongly bitter taste. On account of the intense sweetness of saccharine, this tongue-test must be accepted as decisive, as even the smallest quantity of saccharine in the ethereal residue would be at once manifested by the taste.

Thus the ethereal residue of eleven samples which contain no saccharine on heating with resorcin and concentrated sulphuric acid gave as intense and distinct fluorescence as a sample containing saccharine. This remarkable circumstance led to the conjecture that there is present in beer some compound which behaves with resorcin as does saccharine. Of the constituents of beer which pass into the ethereal extract the most prominent are tannin, the resin, and the bitter principle of the hop. The reaction was first tried with tannin which gave not a trace of fluorescence. It was then tried with a few m.grms. of ordinary colophonium, which gave the same intense green fluorescence as pure saccharine.

The fluorescein reaction therefore cannot be used for the direct recognition of saccharine in the ethereal extract of beer.—*Zeitschrift für Analytische Chemie.*

## ON THE
## EXTRACTION OF ZIRCONIA AND THORIA.

By L. TROOST.

In the Session of the Academy (vol. cxvi., p. 1227) I have shown that zircon (zirconium silicate) heated under the same conditions as zirconia to the temperature of the electric arc produced by a current of 30 to 35 ampères and 70 volts quickly gives long filaments of silica which gradually interlace so as to form a true felt.

As this experiment permits us to get rid of nearly all the silica contained in zirconium silicate, I will detail all its conditions.

The powdered zircon is intimately mixed with an excess of finely sifted charcoal and compressed into small cylinders, which are submitted, on a coke cupel, to the action of the electric arc in a closed vessel traversed by a slow current of carbonic acid. Under these conditions, the production of the filaments of silica is effected rapidly; it is accompanied by a thick black smoke, showing that there is not merely evaporation of the silica, but also, in part, a reduction of the silica by the coke, and consequently the production of pulverulent silicon, which is carried away, and is re-oxidised beyond the electric arc. Hence, along with the evaporation, properly so-called, there is an apparent volatilisation of silica resulting from the double phenomenon of successive reduction and re-oxidation.

In these circumstances, the zircon which before the experiment contained about 33 per cent of silica, leaves a product not containing more than from 1 to 1½ per cent. A part of the zirconia is reduced, and if the furnace is opened before it is completely cold the zirconium resulting from the reduction takes fire, and is re-converted into zirconia. The extraction of zirconia from zircon is thus notably simplified.

If, instead of a mixture of zircon and coke, we expose zircon alone to the temperature of the arc, it melts, but the evaporation of the silica is slow and incomplete, and carries away with it a notable proportion of zirconia.

I have obtained analogous results for the elimination of the silica contained in thorite and orangite (thorium silicate).

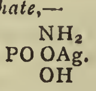
This procedure may be generalised so as to facilitate the preparation of the bases contained in the silicates.—*Comptes Rendus*, cxvi., p. 1428.

## ON AMIDOPHOSPHORIC ACID.[*]

By H. N. STOKES.

(Concluded from p. 19).

*Acid Silver Amidophosphate*,—



$$PO\begin{matrix}NH_2\\OAg.\\OH\end{matrix}$$

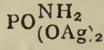
—This may be obtained by precipitating the acid potassium salt with silver nitrate, but, thus obtained, it contains too much silver (about 2 per cent), due, perhaps, to a small amount of neutral salt or to a trace of phosphate. By previously adding a very little nitric acid to the cold solution, it is obtained pure. As it is somewhat soluble in water, the theoretical yield cannot be obtained. It is also formed by dissolving the neutral salt in cold dilute nitric acid and precipitating by alcohol, or by adding alcohol to a solution of the free acid and silver nitrate. It forms a heavy crystalline powder, consisting of short needles, or, oftener, of very thick, short, hexagonal prisms with pyramidal ends, united into groups or twins; also, by precipitating with alcohol, as hexagonal stars. The forms are very characteristic. It is difficultly, but appreciably, soluble in water, easily in dilute nitric or acetic acid, and in ammonia; from the latter solution it crystallises on evaporation. The aqueous solution is at once converted into phosphate by boiling. Light does not discolour it. The air-dried salt is anhydrous. Analysis gave—

| | Calculated for $PO\begin{matrix}NH_2\\OAg.\\OH\end{matrix}$ | Found. |
|---|---|---|
| P .. .. .. | 15·22 | 15·23 |
| Ag .. .. .. | 52·90 | 53·35 |

On ignition it loses ammonia and leaves an easily fusible glass of silver hexametaphosphate.

| | Calculated for $PO\begin{matrix}NH_2\\OAg.\\OH\end{matrix}$ | Found. |
|---|---|---|
| Loss ($NH_3$) .. .. .. | 8·36 | 8·17 |

*Neutral Silver Amidophosphate*,—



$$PO\begin{matrix}NH_2\\(OAg)_2\end{matrix}.$$

—This is obtained either by adding silver nitrate and then ammonia to the filtrate from the acid salt, or (with much loss) by dissolving the acid salts in very dilute nitric acid, and adding silver nitrate and ammonia. It forms at first a turbidity, which in a few moments turns to a quickly subsiding crystalline precipitate. The ammonia must be added cautiously, and stopped as soon as the salt ceases to subside quickly. At this point a nearly white amorphous substance of unknown composition is formed, which remains in suspension, and may be re-dissolved by a drop of nitric acid. Further addition of ammonia to the filtrate gives the same amorphous salt, which is faintly yellow, and rapidly blackens in the light. It may also be obtained from the neutral sodium salt, but this method is not to be recommended, as the product is slightly yellow. The best method is the first mentioned,

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[*] *American Chemical Journal*, vol. xv., No. 3.

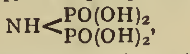
and if very dilute solutions of acid potassium salt have been used, nearly all the acid silver salt remains in solution, and can be converted into neutral salt as described. The neutral salt forms characteristic microscopic rhombic plates, with angles of nearly 60°, often united to bunches. It is colourless and unaffected by light. The crystalline powder is soft, and can thus be distinguished from the acid salt, which is gritty. It is almost insoluble in water; soluble in nitric acid, from which solution alcohol precipitates acid salt; soluble in ammonia, and deposited unchanged on spontaneous evaporation. The air-dried salt is anhydrous.

| | Calculated for $PO.NH_2(OAg)_2$. | Found. | |
|---|---|---|---|
| P .. .. .. | 9·98 | 10·03 | 9·87 |
| N .. .. .. | 4·52 | 4·51 | |
| Ag .. .. .. | 69·40 | 69·18 | 69·15 |

It remains unchanged at 150°; at 180° it loses weight, the loss corresponding to one-half the total nitrogen calculated as ammonia. On heating to constant weight at 180°—

| | Calculated for $2PO.NH_2(OAg)_2—NH_3$. | Found. |
|---|---|---|
| Loss .. .. .. .. | 2·74 | 2·82 |

The residue is brownish, but may be fused over the blast with but slight loss, whereby a little oxygen escapes, and a small amount of metallic silver is formed. In the above case this was weighed, and found to be only 5·61 per cent out of a total of 69·40 per cent. The loss between 180° and red heat was 0·34 per cent, and this is exactly the amount of oxygen which would be given off by the silver oxide corresponding to 5·61 per cent silver. The residue on ignition consists, besides metallic silver, of a yellow glass soluble in ammonia. Probably there is formed at 180° the silver salt of *pyrimidophosphoric acid*,—



$$NH<\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix},$$

which is not decomposed by fusion. Attempt will be made to isolate the free acid.

If the salt be heated at once over the blast, without previous heating at 180°, the decomposition is markedly different, much more metallic silver being formed.

| | Calculated for $\frac{1}{2}N$ as $NH_3$. | Found. |
|---|---|---|
| Loss .. .. .. .. .. | 2·74 | 4·63 |
| Free silver.. .. .. | — | 25·75 |

This amount of silver corresponds to 1·91 per cent oxygen, which with 2·74 per cent ammonia makes 4·65 per cent loss, the amount actually found. The formation of silver oxide is due to the liberated ammonia, which splits off silver oxide and water, forming a higher amide. The action of dry ammonia gas on the salt is scarcely appreciable at 180°, as was found by experiment, hence the salt may be heated at this temperature without the ammonia which is given off liberating any considerable amount of silver oxide, as seen in the first case. At 200° and higher, dry ammonia forms large amounts of silver oxide and water, and therefore on heating rapidly, as in the second case, the liberated ammonia is able to act, and the large amount of silver formed is accounted for. The products of the action of dry ammonia on this salt will be described in a future article, when it will also be shown that amidophosphates may be made from neutral silver phosphate in this way. Experiments towards forming other inorganic amides by this method are also in progress.

### *Free Amidophosphoric Acid.*

The isolation of the free acid is attended with difficulties, owing to its unstable nature. It has not yet been obtained perfectly pure, and the yield is always far below the theoretical. The silver salts may be decomposed by hydrochloric acid in the cold, and the solution precipitated by alcohol, but a deficiency of acid causes the solution to be contaminated with acid salt, and an excess destroys the amido-acid completely, or at least prevents its precipitation. The decomposition of the silver salts by sulphuretted hydrogen gives better, but unsatisfactory, results. The best results are obtained by suspending the lead salt in a little ice-water, and decomposing by sulphuretted hydrogen. It is essential to have the latter in excess, as otherwise the solution contains some lead salt. The filtrate is run into four or five volumes of alcohol, whereby the acid is at once precipitated in the form of microscopic crystals. These consist sometimes of thick plates, sometimes of forms which appear to be cubes, but which are anisotropic. It is insoluble in alcohol, easily soluble in water, the solution having a sweetish taste. It gives no precipitate with silver nitrate, unless on addition of ammonia or alcohol. It evolves no ammonia with caustic alkalis, and is easily converted into the characteristic sodium, magnesium, barium, and silver salts, hence there can be no question as to its nature. It may be exposed to the air for a long time without change, but gradually alters, becoming pasty, in which condition it precipitates silver nitrate directly, and hence has become converted into an ammonium salt. The precipitate is white and amorphous, hence not phosphate. Its solution, if boiled but a moment, also gives a white silver precipitate, but on boiling several minutes it is completely converted into phosphate. It does not lose weight at 100°, but is slowly converted into ammonium salt, giving a white silver precipitate direct. Whether the product is one of the isomeric ammonium metaphosphates has not yet been determined. At 150° it also loses nothing, but fuses partially, and on higher heating it gives off ammonia. The silver salt from the acid which has been heated just to fusion becomes pasty under boiling water, like silver hexametaphosphate. The free acid obtained as above did not give satisfactory results on analysis, and such data are therefore postponed.

The alcoholic filtrate from the free acid contains an abundance of ammonium salts, giving amorphous, white, silver precipitates.

The action of amidophosphoric acid towards indicators is not sharp. The free acid gives acid reaction, the acid alkali salts have neutral reaction, but no sharp transitions can be obtained either with litmus, methyl orange, or phenolphthalein. It also differs from phosphoric acid in the uniformity with which its acid alkali salts precipitate acid salts, and its neutral alkali salts give neutral salts. No exception to this was observed. Soluble acid phosphates, as is well known, give, with silver and many other metals, precipitates of neutral salt.

The investigation will be continued in the directions indicated.

The above data were worked out, for the most part, in the chemical laboratory of the United States Geological Survey, in Washington, and I am indebted to the director, Major Powell, and to Professor F. W. Clarke for the opportunity of so doing.

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**Determination of Total Nitrogen in Urine.**—C. Arnold and K. Wedemeyer (*Pflüger's Archiv*).—The authors compared the time required for the complete decomposition of urine on Kjeldahl's process if they used a mixture of 1 part potassium sulphate and 2 parts sulphuric acid, or sulphuric acid with 1 grm. each mercury and copper sulphate, or the exclusive use of one of the latter additions. In all three cases the oxidation was equally rapid, but in presence of potassium sulphate the frothing was stronger, unless sulphuric acid was added in excess. Arnold and Wedemeyer condemn the process of Schneider-Sugen, as less convenient and less accurate.

# POLARISATION OF PLATINUM ELECTRODES IN SULPHURIC ACID.*

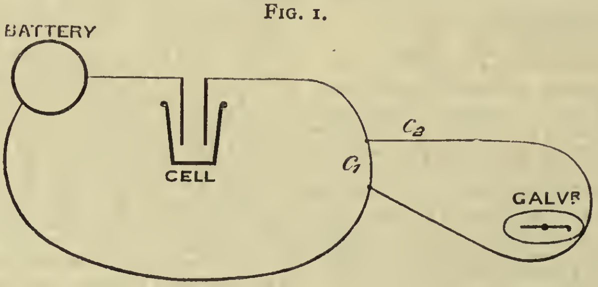
By JAMES B. HENDERSON, B.Sc.

This investigation was begun about the beginning of February, 1893, at the instigation of Lord Kelvin, and was conducted in the Physical Laboratory of Glasgow University. The object of the investigation was to obtain the difference of potential between two platinum electrodes immersed in a solution of sulphuric acid immediately after the stoppage of a current which had been electrolysing the solution, and to find how this difference varied with a variation in the intensity of the current or in the strength of the solution.

Former experiments by Buff (*Poggendorff*, vol. cxxx., p. 341, 1867) and Fromme (*Wiedemann*, vol. xxxiii., p. 80, 1888) have given for the maximum polarisation with platinum wires of very small surface in the electrolysis of dilute sulphuric acid 3·5 and 4·6 volts.

Dr. Franz Richarz, in a paper "On the Polarisation of Small Electrodes in Dilute Sulphuric Acid," read before the British Association at Bath (1888), says of the above:—

FIG. 1.

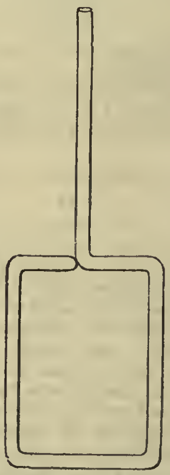


"In these experiments the polarisation is calculated from measurements of the intensity of the galvanic current during the electrolysis, tacitly assuming that the resistance of the decomposition cell is independent of the intensity of the galvanic current. The correctness of the supposition has not been proved. I tried experiments by similar methods, and obtained yet greater values of the polarisation; it was calculated with a current density of 12 ampères per square centimetre as 4·4 daniells (4·7 volts), and increased more and more with increasing intensity of the galvanic current. It is very improbable that this can be right. By supposing, however, that the resistance of the decomposition cell is not independent of the intensity, but decreases in a fixed manner with increasing intensity, the calculation of the same experiment gives small and constant values of polarisation."

The method Dr. Richarz used to find the polarisation in his investigation was independent of the resistance of the electrolytic cell. The battery electrolytic cell and a switch, $c_1$, were joined in closed circuit, A branch circuit containing a very high resistance, a galvanometer, and another switch, $c_2$, joined the two sides of the switch $c_1$ ($c_1$ and $c_2$ were the two contacts of a Hemholtz's pendulum interrupter). When $c_1$ was made there was a very small current through the galvanometer. To determine the polarisation, $c_1$ was broken, and immediately after $c_2$ also. In the short time between the interruption of $c_1$ and $c_2$ a current strong for the sensibility of the galvanometer went through it. The polarisation was calculated from the deflection given to the galvanometer needle by the impact of the current, which was proportional to the electromotive force of the battery *minus* the polarisation. In this way, Dr. Richarz found values for the polarisation never greater than 2·6 volts with small wire electrodes, and also got the same maximum with large platinum plates.

The cell used in the present investigation was a cylindrical glass vessel 10 c.m. diameter and 12 c.m. deep. The electrodes were rectangular plates of platinum foil, 7 c.m. long by 5·5 c.m. broad, and were stiffened by being mounted on rectangular frames made by bending glass tubing (Fig. 2). The tubing of these frames also served to support the plates in vertical planes by being passed through holes in a bar of wood placed across the mouth of the vessel. The plates were immersed in the solution to a depth of 5 c.m., having their planes parallel and about 1 c.m. apart. There were thus 55 sq. c.m. of surface of each plate wetted. To find the polarisation one of Lord Kelvin's quadrant electrometers were used, and by an arrangement, described later, the breaking of the electrolysing current circuit and the switching of the electrodes on to the terminals of the electrometer were done simultaneously. Before switching as above, however, the needle of the electrometer was deflected by making a difference of potential between the pairs of quadrants, and this deflection was so adjusted by trial and error that, when the electrodes were switced on, the needle was no further deflected. For deflecting the needle of the electrometer a high resistance slide bridge was used. A difference of potential was maintained between its two ends, and the difference of potential between one end and the slider was used to deflect the needle, so that by moving the slider one way or the other the deflection could be increased or diminished at will. The electrolysing current was kept constant throughout each experiment, being measured by one of Lord Kelvin's electric balances and adjusted by a rheostat. One terminal of the electrometer, one electrode, and one end of the slide bridge were connected together and then put to earth. The current for the electrolysis was got from eight large

FIG. 2.



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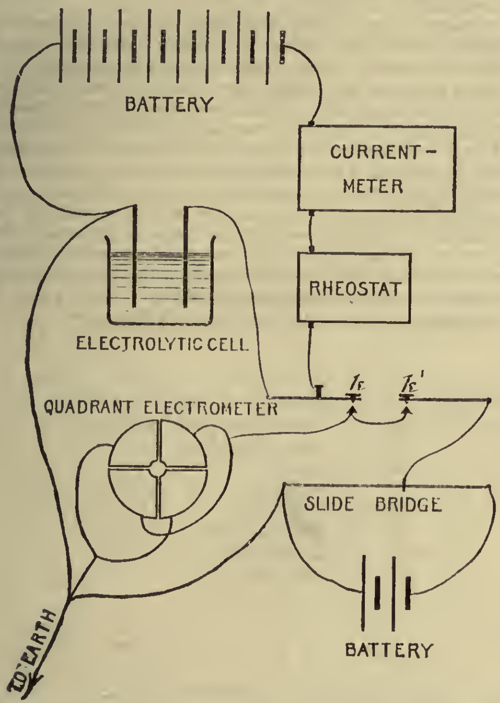
* A Paper read before the Royal Society, June 15, 1893.

secondary cells, and the difference of potential between the ends of the slide bridge was maintained by two small secondary cells. The arrangement of keys can be best understood from the diagram. By pressing the key $k'$, connection was made between the slider and the unearthed quadrants, and when the key $k$ was free, the circuit was complete for the electrolysing current, but when $k$ was pressed down the circuit was broken, and the unearthed electrode was connected to the unearthed quadrants.

Fig. 3.



The order of an experiment was the following:—

After carefully standardising the electrometer, the electrolysis was started and the unearthed electrode connected by a wire (not shown in the diagram) to the unearthed quadrants. The deflection of the needle thus produced, which showed the difference of potential between the electrodes, continued to increase steadily until, after the lapse of an interval of time depending on the strength of the current, it became constant. When this stage was reached the wire mentioned above was removed and the key $k'$ pressed and kept down, thus making connection between the slider and the quadrants. The slider was then moved along until the deflection was nearly equal to that which would be given by the polarisation, and the key $k$ momentarily pressed, thereby breaking the current circuit and connecting the electrode to the quadrants. An impulsive deflection immediately followed, unless the potential of the quadrants was equal to that of polarisation. If this deflection was negative (which indicated that the potential of polarisation was less than that of the quadrants) the slider was moved so as to reduce the potential of the quadrants below that of polarisation, thereby making the impulsive deflection positive, and then the experiment was continued as below. When the positive deflection was obtained its amount was noted, and the slider was moved so as to increase the steady deflection nearly up to the point on the scale reached by the impulsive one, and another trial then made. In this way, by watching the point reached by each impulsive deflection, and then increasing the steady one almost up to that point, the latter was increased until the former vanished, that is, until the potential of the quadrants was that of polarisation. The magnitude of this deflection was then noted, and the polarisation calculated from it. In these trials the key $k$ was kept down only for about two seconds, just sufficient time to allow the extent of the deflection to be seen, and at least two minutes were allowed to elapse between one trial and the next.

After the maximum deflection had been reached, a considerable interval of time was allowed to elapse, and then the key $k'$ raised and $k$ simultaneously lowered and kept down, and the rate of fall of the deflection noted. The above motion of the keys threw the slider off and put the electrode on to the quadrants, at the same time stopping the current. The deflection was therefore due to polarisation alone, and its rate of fall was therefore the rate of fall of the polarisation.

The results of one series of experiments are given in the accompanying Table.

All the results point to the polarisation being constant with large electrodes, being independent of the strength of the solution and the intensity of the current. The variations in the figures do not occur in any order, and are all such as might be expected in experimental results of this nature. Some of the greatest variations were obtained in exactly similar experiments performed at different times.

The mean of all the values of the polarisation in this Table is 2·09 volts.

The rate of fall of the polarisation depends on the time the current has been electrolysing the solution, and also on its intensity, but in every case the fall is very rapid at first, being in some cases as much in the first minute as it is in the next five minutes, and the fall in the first minute is never less than one-fourth of the polarisation.

| Percentage strength of solution. | Strength of current in ampères. | Time the current had been passing. | | Polarisation in volts. |
|---|---|---|---|---|
| | | H. | M. | |
| 30 | 0·2 | 3 | 25 | 2·066 |
| 30 | 0·5 | 0 | 45 | 2·060 |
| 30 | 1·0 | 0 | 35 | 2·060 |
| 30 | 1·0 | 0 | 45 | 2·124 |
| 20 | 0·1 | 3 | 22 | 2·126 |
| 20 | 0·5 | 1 | 25 | 2·139 |
| 20 | 1·0 | 0 | 25 | 2·090 |
| 20 | 1·0 | 0 | 35 | 2·124 |
| 10 | 0·1 | 17 | 40 | 2·139 |
| 10 | 0·5 | 1 | 19 | 2·066 |
| 10 | 1·0 | 0 | 44 | 2·066 |
| 5 | 0·1 | 18 | 30 | 2·116 |
| 5 | 0·5 | 1 | 36 | 2·078 |
| 5 | 1·0 | 1 | 0 | 2·083 |
| 5 | 1·0 | 3 | 15 | 2·054 |

Mean polarisation = 2·09 volts.

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 23).

In a previous page I assumed that we had reduced the chemical constituents of a mineral to the form of soluble sulphates, and had crystallised a mixture of these sulphates on glass slides for microscopic examination. An inspection of these slides, with the information contained in Part II. before us, will often give us important information regarding the character of the mineral under examination. For instance, if we have treated a piece of serpentine in the manner described it will be at once seen that the principal chemical constituent of the mine-

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* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

ral is magnesia, for unmistakable crystals of magnesium sulphate will occupy a prominent position on the slide. But supposing that we wish to confirm this determination, or to ascertain what other sulphates are contained in our solution, we can pass on to the reactions based on Part II., or to those detailed in Part III.

The double sulphates, recorded in Part II., supply us with a valuable means of detecting the presence of many metallic salts. Suppose, for instance, that we are seeking for evidence of the presence of sodium, we examine our original slides to see whether they contain any cubic crystals of alum. If they do not do so, there is a strong probability that the mineral under examination does not contain either aluminium or chromium as well as sodium. We then place a few drops of the original aqueous solution on several glass slides and add two or three drops of an aqueous solution of aluminium sulphate to some of the slides, and two or three of chromic sulphate to the other slides, and allow these to evaporate spontaneously without the application of heat. If soda be present in the mineral, crystals of alum will be found on the slides.

Then we can further test for soda (without going beyond methods based on Part II.) by employing, in the way described, the sulphates of calcium, magnesium, or manganese, with each of which sodium sulphate forms double salts.

The above illustration refers to the detection of sodium only, but a reference to Part II. will show that the sulphates of many other metals may be detected by the employment of sulphates that form double salts with them. Cold solutions, combined with spontaneous evaporation, have yielded me the best results.

In Part III. I have given some selected tests *supplementary* to those suggested by Part II. Most of these reactions, due originally to Haushofer, Behrens, Boricky, and others, have been taken from the works of Klement and Renard ("Reactions Microchimiques," par C. Klement et A. Renard, 1886), and Behrens ("Contributions to Micro-chemical Analysis," by H. Behrens; Chemical News, 1891). I have tried and can recommend all the reactions entered in Part III. In one or two cases I have given my reasons for rejecting some reactions that have been suggested by various authorities; but I think it unnecessary to specify my grounds for excluding other reactions which I have tried, but which, from their requiring great heat, great expertness on the part of the operator. or reagents that I could not obtain sufficiently pure, or for some other reason, were found unsuitable for ordinary use.

In Part III. I have noted facts that seem to me of interest regarding some of the salts alluded to therein, and I will now conclude with a few observations of more general character.

Several interesting facts will be apparent on a consideration of Part II. The first is that the addition of a single molecule of water to the formula of a hydrate is sufficient, in some cases, to completely alter the physical properties of the salt, involving not only a change in its optical properties, and in its solubility, but in some cases even a change of colour.

Conversely the loss of water, even when heat has not been employed, may result in a change of molecular structure, as in the interesting instance noted in Part III., iron, where a salt changes from a glass into a crystal on losing some of its water.

The formation of one hydrate rather than another depends in some cases on the temperature at which crystallisation takes place, and in others on other considerations—solubility being probably a dominating factor. That is to say, as evaporation proceeds, and the volume of water present is reduced, one hydrate may be thrown down first and another later on.

The student may sometimes be disconcerted by the diversity of forms presented to him by micro-chemical reactions; but fundamental diversity of form in such cases is, I suspect, more often the result of minute difference in chemical composition than an instance of polymorphism. Hydrates, basic salts, or double salts, of which little or nothing is yet known, may be formed under special conditions. These salts reveal themselves under the microscope in forms that are new to the student, and invite him to future excursions into unexplored fields of research.

Another thing that has interested me as a student of igneous rocks is the presence in these salts of aqueous origin of twinning, zonal structure, and cleavage lines.

Many kinds of twinning—penetration twins, ordinary binary twins, and polysynthetic twinning, combined with macles analogous to those on the pericline plan—are to be found in crystals formed on glass slides in the manner above described, and they appear to be congenital in origin. They are by no means confined to crystals formed round the margin of a drop, where it might possibly be alleged that they had suffered strains from molecular tension, or from crowding; but they appear quite as commonly in discrete crystals standing by themselves in the centre of the area originally covered by the liquid.

The following abbreviations are used in Part II. :—

| | | |
|---|---|---|
| *R.L.* | for | right angle. |
| ‖ | ,, | parallel. |
| *e* | ,, | direction of elongation. |
| *c.p.l.* | ,, | converging polarised light. |
| *Q.W.* | ,, | quartz wedge. |
| *C.* | ,, | cubic. |
| *T.* | ,, | tetragonal. |
| *H.* | ,, | hexagonal. |
| *R.* | ,, | orthorhombic. |
| *M.* | ,, | monoclinic. |
| *Tr.* | ,, | triclinic. |

(To be continued).

## TURACIN, A REMARKABLE ANIMAL PIGMENT CONTAINING COPPER.*

By Prof. A. H. CHURCH, M.A., F.R.S.

The study of natural colouring-matters is at once peculiarly fascinating and peculiarly difficult. The nature of the colouring-matters in animals and plants, and even in some minerals (ruby, sapphire, emerald, and amethyst, for example), is still, in the majority of cases, not completely fathomed.

Animal pigments are generally less easily extracted and are more complex than those of plants. They appear invariably to contain nitrogen—an observation in accord with the comparative richness in that element of animal cells and their contents. Then, too, much of the colouration of animals, being due to microscopic structure, and therefore having a mechanical and not a pigmentary origin, differs essentially from the colouration of plants. Those animal colours which are primarily due to structure do, however, involve the presence of a dark pigment—brown or black—which acts at once as a foil and as an absorbent of those incident rays which are not reflected.

Many spectroscopic examinations of animal pigments have been made. Except in the case of blood- and bile-pigments, very few have been submitted to exhaustive chemical study. Spectral analysis, when uncontrolled by chemical, and when the influence of the solvent employed is not taken into account, is very likely to mislead the investigator. And, unfortunately, the non-crystalline character of many animal pigments, and the difficulty of purifying them by means of the formation of salts and of separations by the use of appropriate solvents, oppose

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* A Lecture delivered at the Royal Institution of Great Britain, Friday, February 17th, 1893.

serious obstacles to elucidation. Of blood-red or hæmoglobin it cannot be said that we know the centesimal composition, much less the molecular weight. Even of hæmatin the empirical formula has not yet been firmly established. The group of black and brown pigments to which the various melanins belong still awaits adequate investigation. We know they contain nitrogen ($8\frac{1}{2}$ to 13 per cent, and sometimes iron, but the analytical results do not warrant the suggestion of empirical formulæ for them. The more nearly they appear to approach purity the freer the majority of them seem from any fixed constituent such as iron or other metal. It is to be regretted that Dr. Krukenberg, to whom we are indebted for much valuable work on several pigments extracted from feathers, has not submitted the interesting substances he has described to quantitative chemical analysis.

I must not, however, dwell further upon these preliminary matters. I have introduced them mainly in order to indicate how little precise information has yet been gathered as to the constitution of the greater number of animal pigments, and how difficult is their study.

And now let me draw your attention to a pigment which I had the good fortune to discover, and to the investigation of which I have devoted I am afraid to say how many years.

It was so long ago as the year 1866 that the solubility in water of the red colouring-matter in the wing-feathers of a *plantain-eater* was pointed out to me. [One of these feathers, freed from grease, was shown to yield its pigment to pure water.] I soon found that alkaline liquids were more effective solvents than pure water, and that the pigment could be precipitated from its solution by the addition of an acid. [The pigment was extracted from a feather by very dilute ammonia, and then precipitated by adding excess of hydrochloric acid.] The next step was to filter off the separated colouring-matter, and to wash and dry it. The processes of washing and drying are tedious, and cannot be shown in a lecture. But the product obtained was a solid of a dark crimson hue, non-crystalline, and having a purple semi-metallic lustre. I named it *turacin* (in a paper published in a now long-defunct periodical, *The Student and Intellectual Observer*, of April, 1868). The name was taken from "*Touraco*," the appellation by which the *plantain-eaters* are known —the most extensive genus of this family of birds being *Turacus*.

From the striking resemblance between the colour of arterial blood and that of the red touraco feathers, I was led to compare their spectra. Two similar absorption-bands were present in both cases, but their positions and intensities differed somewhat. Naturally I sought for iron in my new pigment. I burnt a portion, dissolved the ash in hydrochloric acid, and then added sodium acetate and potassium ferrocyanide. To my astonishment I got a precipitate, not of Prussian blue, but of Prussian brown. This indication of the presence of copper in turacin was confirmed by many tests, the metal itself being also obtained by electrolysis. It was obvious that the proportion of copper present in the pigment was very considerable—greatly in excess of that of the iron (less than 0·5 per cent) in the pigment of blood.

Thus far two striking peculiarities of the pigment had been revealed, namely, its easy removal from the web of the feather, and the presence in it of a notable quantity of copper. Both facts remain unique in the history of animal pigments. The solubility was readily admitted on all hands, not so the presence of copper. It was suggested that it was derived from the Bunsen burner used in the incineration, or from some preservative solution applied to the bird-skins. And it was asked, "How did the copper get into the feathers?" The doubters might have satisfied themselves as to copper being normally and invariably present by applying a few easy tests and by the expenditure of half-a-crown in acquiring a touraco wing. My results were, however, confirmed (in 1872) by several independent observers, including Mr. W. Crookes, Dr. Gladstone, and Mr. Greville Williams. And in 1873 Mr. Henry Bassett, at the request of the late Mr. J. J. Monteiro, pushed the inquiry somewhat further. I quote from Monteiro's "Angola and the River Congo," published in 1875 (vol. ii., pp. 75—77). "I purchased a large bunch of the red wing-feathers in the market at Sierra Leone, with which Mr. H. Bassett has verified Professor Church's results conclusively," &c., &c. Mr. Bassett's results were published in the CHEMICAL NEWS in 1873, three years after the appearance of my research in the *Phil. Trans.* As concentrated hydrochloric acid removes no copper from turacin, even on boiling, the metal present could not have been a mere casual impurity; as the proportion is constant in the turacin obtained from different species of touraco, the existence of a single definite compound is indicated. The presence of traces of copper in a very large number of plants, as well as of animals, has been incontestably established. And, as I pointed out in 1868, copper can be readily detected in the ash of banana fruits, the favourite food of several species of the "turacin-bearers." The feathers of a single bird contain on the average 2 grains of turacin, corresponding to 0·14 of a grain of metallic copper; or, putting the amount of pigment present at its highest, just one-fifth of a grain. This is not a large amount to be furnished by its food to one of these birds once annually during the season of renewal of its feathers. I am bound, however, to say that in the blood and tissues of one of these birds, which I analysed immediately after death, I could not detect more than faint traces of copper. The particular specimen examined was in full plumage; I conclude that the copper in its food, not being then wanted, was not assimilated.

Let us now look a little more closely at these curious birds themselves. Their nearest allies are the cuckoos, with which they were formerly united by systematists. It has, however, been long conceded that they constitute a family of equal rank with the Cuculidæ. According to the classification adopted in the Natural History Museum the order Picariæ contains eight sub-orders, the last of which, the Coccyges, consists of two families, the Cuculidæ and the Musophagidæ. To the same order belong the Hoopoes, the Trogons, the Woodpeckers. The plantain eaters or Musophagidæ are arranged in six genera and comprise twenty-five species. In three genera—Toracus, Gallirex, and Musophaga—comprising eighteen species, and following one another in zoological sequence, turacin occurs; from three genera (seven species)—Corythæola, Schizorhis, and Gymnoschizorhis—the pigment is absent. [The coloured illustrations to H. Schlegel's Monograph (Amsterdam, 186c) on the Musophagidæ were exhibited.] The family is confined to Africa; eight of the turacin-bearers are found in the west sub-region, one in the south-west, two in the south, two in the south-east, four in the east, two in the central, and two in the north-east. It is noteworthy that, in all these sub-regions save the south-east, turacin-bearers are found along with those plantain-eaters which do not contain the pigment. Oddly enough two of the latter species, *Schizorhis africana* and *S. zonura*, possess white patches destitute of pigment in those parts of the feathers which in the turacin-bearers are crimson. These birds do not—I will not say cannot—decorate these bare patches with this curiously complex pigment. [Some extracts were here given from the late Mr. Monteiro's book on Angola (vol. ii., pp. 74—79), and from letters by Dr. B. Hinde. These extracts contained references to curious traits of the touracos.]

Usually from twelve to eighteen of the primaries or metacarpo-digitals and secondaries or cubitals, amongst the wing-feathers of the turacin-bearers have the crimson patches in their web. Occasionally the crimson patches are limited to six or seven of the eleven primaries. I have observed this particularly with the violet plantain-eater (*Musophaga violacea*). In these cases the crimson head-feathers, which also owe their colour to turacin, are few in number, as if the bird, otherwise healthy, had been unable to manufacture a sufficiency of the pigment. I may here add that the red tips of the crest-feathers of *Turacus meriani* also contain turacin.

In all the birds in which turacin occurs this pigment is strictly confined to the red parts of the web, and is there unaccompanied by any other colouring-matter. It is therefore found that if a single barb from a feather be analysed, its black base and its black termination possess no copper, while the intermediate portion gives the blue-green flash of copper when incinerated in the Bunsen flame. [A parti-coloured feather was burnt in the Bunsen flame, with the result indicated.

Where it occurs, turacin is homogeneously distributed in the barbs, barbicels, and crochets of the web, and is not found in granules or corpuscles.

To the natural question "Does turacin occur in any other birds besides the touracos?" a negative answer must at present be given. At least my search for this pigment in scores of birds more or less nearly related to the Musophagidæ has met with no success. In some of the plantain-eaters (species of Turacus and Gallirex) there is, however, a second pigment closely related to turacin. It is of a dull grass-green colour, and was named Turacoverdin by Dr. Krukenberg in 1881. I had obtained this pigment in 1868 by boiling turacin with a solution of caustic soda, and had figured its characteristic absorption-band in my first paper (*Phil. Trans.*, vol. clix., 1870, p. 630, fig. 4). My product was, however, mixed with unaltered turacin. But Dr. Krukenberg obtained what certainly seems to be the same pigment from the green feathers of *Turacus corythaix*, by treating them with a 2 per cent solution of caustic soda. I find, however, that a solution of this strength dissolves, even in the cold, not only a brown pigment associated with turacoverdin, but ultimately the whole substance of the web. By using a much weaker solution of alkali (one part to a thousand of water) a far better result is obtained. [The characteristic absorption-band of turacoverdin, which lies on the less refrangible side of D, was shown; also the absorption-bands of various preparations of turacin.] I have refrained from the further investigation of turacoverdin, hoping that Dr. Krukenberg would complete his study of it. At present I can only express my opinion that it is identical with the green pigment into which turacin when moist is converted by long exposure to the air or by ebullition with soda, and which seems to be present in traces in all preparations of *isolated* turacin, however carefully prepared.

A few observations may now be introduced on the physical and chemical characters of turacin. It is a colloid of colloids. And it enjoys in a high degree one of the peculiar properties of colloids, that of retaining, when freshly precipitated, an immense proportion of water. Consequently, when its solution in ammonia is precipitated by an acid, the coagulum formed is very voluminous. [The experiment was shown.] One grm. of turacin is capable of forming a semi-solid mass with 600 grms. of water. Another character which turacin shares with many other colloids is its solubility in pure water and its insolubility in the presence of mere traces of saline matter. It would be tedious to enumerate all the observed properties of turacin, but its deportment on being heated and the action of sulphuric acid upon it demand particular attention.

At 100° C., and at considerably higher temperatures, turacin suffers no change. When, however, it is heated to the boiling-point of mercury it is wholly altered. No vapours are evolved, but the substance becomes black and is no longer soluble in alkaline liquids, nor, when still more strongly heated afterwards, can it be made to yield the purple vapours which unchanged turacin gives off under the same circumstances. This peculiarity of turacin caused great difficulty in its analysis, for these purple vapours contain an organic crystalline compound in which both nitrogen and copper are present, and which resist further decomposition by heat. [Turacin was so heated as to show its purple vapours, and also the green flame with which they burn.] This production of a volatile organic compound of copper is perhaps comparable with the formation of nickel- and ferro-carbonyl.

The action of concentrated sulphuric acid upon turacin presents some remarkable features. The pigment dissolves with a fine crimson colour, and yields a new compound, the spectrum of which presents a very close resemblance to that of hæmatoporphyrin [Turacin was dissolved in oil of vitriol; the spectrum of an ammoniacal solution of the turacoporphyrin thus produced was also shown], the product obtained by the same treatment from hæmatin; in other respects also this new derivative of turacin, which I call turacoporphyrin, reminds one of hæmatoporphyrin. But, unlike this derivative of hæmatin, it seems to retain some of its metallic constituent. The analogy between the two bodies cannot be very close, for if they were so nearly related as might be argued from the spectral observations, hæmatin ought to contain not more but less metal than is found to be present therein.

The percentage composition of turacin is probably:—Carbon, 53·69; hydrogen, 4·6; copper, 7·01; nitrogen, 6·96; and oxygen, 27·74. These numbers correspond pretty nearly to the empirical formula, $C_{82}H_{81}Cu_2N_9O_{32}$. But I lay no stress upon this expression.

I have before said that copper is very widely distributed in the Animal Kingdom. Dr. Giunti, of Naples, largely extended (1881) our knowledge on this point. I can hardly doubt that this metal will be found in traces in all animals. But besides turacin only one organic copper compound has been as yet recognised in animals. This is a respiratory, and not a mere decorative, pigment like turacin. Léon Fredericq discovered this substance, called hæmocyanin. It has been observed in several genera of Crustacea, Arachnida, Gastropoda, and Cephalopoda. I do not think it has ever been obtained in a state of purity, and I cannot accept for it the fantastic formula—$C_{867}H_{1369}CuS_4O_{258}$—which has recently been assigned to it. On the other hand, I do not sympathise with the doubts as to its nature which F. Heim has recently formulated in the *Comptes Rendus*.

It is noteworthy, in connection with the periodic law, that all the essential elements of animal and vegetable organic compounds have rather low atomic weights,—iron, manganese, and copper representing the superior limit. Perhaps natural organic compounds containing manganese will some day be isolated, but at present such bodies are limited to a few containing iron, and to two—hæmocyanin and turacin—of which copper forms an essential part.

If I have not yet unravelled the whole mystery of the occurrence and properties of this strange pigment, it must be remembered that it is very rare and costly, and withal difficult to prepare in a state of assured purity. It belongs, moreover, to a class of bodies which my late master, Dr. A. W. von Hofmann, quaintly designated as "dirts" (a magnificent dirt truly!)—substances which refuse to crystallise and cannot be distilled. I have experienced, likewise, during the course of this investigation, frequent reminders of another definition propounded by the same great chemist, when he described organic research as "a more or less circuitous route to the sink"!

I am very glad to have had the opportunity of sharing with an audience in this Institution the few glimpses I have caught from time to time during the progress of a tedious and still incomplete research into the nature of a pigment which presents physiological and chemical problems of high if not of unique interest.

Let my last word be a word of thanks. I am indebted to several friends for aid in this investigation, and particularly to Dr. MacMunn, of Wolverhampton, the recognised expert in the spectroscopy of animal pigments.

# THE PROBABLE DESTRUCTION OF BACTERIA IN POLLUTED RIVER WATER BY INFUSORIA.*

By D. HARVEY ATTFIELD, M.A., M.B., B.C., D.Ph., Cantab., Demonstrator in the Public Health Laboratories, King's College.

Towards the end of June, 1892, Professor Dr. Emmerich, of the Hygienic Institute of the Royal University of Munich, suggested that possibly infusoria had something to do with that self-purification of impure water which is well known to occur in many circumstances. With the object of investigating this matter I carried on the following series of experiments in the laboratories of the Institute:—

On July 1st two 1-litre flasks, which may be designated A and B, were sterilised. Into each of these was introduced about 500 c.c. of water drawn from a certain disused well. This water contained an average of 10,000 bacteria per c.c., as estimated by counting the colonies on gelatin plates in the usual manner, but was almost free from infusoria. To A was added 10 c.c. of River Isar water. The latter was collected about 150 metres below the influx of one of the main Munich sewers. The Isar water contained much *Beggiatoa alba*, and swarmed with infusoria as well as with the bacteria of the sewage. The infusoria were for the most part *Paramœcia aurelia* and *P. caudatum*. After diluting a portion of A with sterilised water three gelatin plates were made containing respectively:—

(1) 0·008 c.c. of A. (2) 0·016 c.c. of A. (3) 0·024 c.c. of A.

Three plates were also made from the contents of B—that is, the well water without Isar water:—

(1) 0·010 c.c. of B. (2) 0·020 c.c. of B. (3) 0·050 c.c. of B.

The plates and the two flasks were then placed in the cellar of the Institute, because the temperature there resembled that of the well from which the water was drawn.

July 2nd.—No colonies were as yet found on the plates. The infusoria in A were observed to be in active movement. More plates were prepared from A and B.

July 4th.—From the counting of the colonies on the plates prepared on July 1st—

A had 259,000 bacteria per c.c.
B had 10,000 bacteria „

Additional plates were made from A and B. The plates prepared from A on July 2nd showed that A had on that day an average of 364,000 bacteria per c.c.

July 5th.—The plates made on July 4th had not developed sufficiently for counting the colonies. Further plates were prepared from A and B.

July 6th.—The plates made from A on July 4th showed 48,500 bacteria per c.c.

July 8th.—The plates made on July 5th from A showed a bacterial contents of 47,500 per c.c.; from B, 5,450.

These results may be thus tabulated:—

A, 10,000 *Bacteria per C.c.—Isar Water Added.*

| | | |
|---|---|---|
| July 1st, per c.c. | .. .. | 259,000 bacteria. |
| „ 2nd „ | .. .. | 364,000 „ |
| „ 4th „ | .. .. | 48,500 „ |
| „ 5th „ | .. .. | 47,500 „ |

B, 10,000 *Bacteria per C.c.—No Isar Water Added.*

| | | |
|---|---|---|
| July 1st, per c.c. | .. .. | 10,000 bacteria. |
| „ 5th „ | .. .. | 5,450 „ |

It thus appears that in the water (A) swarming with infusoria, the bacteria had decreased to less than one-fifth of their original number in six days; whereas in the water (B) containing very few, if any, infusoria, the decrease of the bacteria in six days was only one-half of their original number.

I now made another series of experiments, using in the one case Isar water taken from *above*, and, in the other, from *below*, a point of inflow of sewage. A suggestion having been made that in the previous experiments perhaps light had something to do with the destruction of the bacteria—for a certain amount of direct sunlight had access to the cellar—in this series of experiments similarly prepared vessels were protected from light by means of appropriate covers of black cardboard.

The contents of the two bottles were kept in constant movement by blowing a slow current of air through each bottle by means of a forcing air-pump, the air being filtered through plugs of sterilised cotton-wool. The water used was, for A, collected 150 metres below the influx of the main Munich sewer into the Isar. It contained some *Beggiatoa alba* and infusoria. For B, the water was collected, as I have said, from the Isar above Munich. The methods of procedure, namely, making plate cultures and counting the colonies, were carried out as in the previous series of experiments.

The figures obtained from these results may be tabulated as follows:—

A.—Isar water from below Munich with a little *Beggiatoa alba* and many *Paramœcia*.

B.—Isar water from above Munich, containing no apparent infusoria.

A.

| | | Bacteria per c.c. |
|---|---|---|
| Plates of July 11 | .. .. .. | 637,000 |
| „ „ 13 | .. .. .. | 462,000 |
| „ „ 14 | .. .. .. | 3,300 |
| „ „ 15 | .. .. .. | 11,000 |
| „ „ 16 | .. .. .. | 1,200 |

B.

| | | Bacteria per c.c. |
|---|---|---|
| Plates of July 11 | .. .. .. | 5,900 |
| „ „ 13 | .. .. .. | 23,800 |
| „ „ 14 | .. .. .. | 33,300 |
| „ „ 15 | .. .. .. | 26,500 |
| „ „ 16 | .. .. .. | 2,000 |

In all these cases, with one exception, the plates were counted after from thirty-six to forty-eight hours. The exception is that of the A plates dated July 15th, when, owing to unavoidable absence, the counting was not done till about seventy-two hours after preparation; hence, perhaps, the increase noted.

Here again the proportional amount of decrease of bacteria between the water with infusoria and that without them will be observed to be very marked. In A the decrease is from 637,000 to 1200,—that is, as from 500 to 1,—while in B it is from 33,300 to 2000—that is, nearly 17 to 1.

On July 19 a fresh series of experiments was started. As before, samples of water from below Munich with infusoria and from above the town without them were collected in sterilised bottles.

In this series, however, each water, A and B, was divided into two equal portions, which may be designated as $A_1$ and $A_2$, and $B_1$ and $B_2$; the two former being from below and the two latter from above Munich, as before. At the time of taking these samples the Isar was in flood, and in consequence the water was very turbid from suspended matter. Through $A_1$ and $B_1$ air was blown, while $A_2$ and $B_2$ were not so treated.

From these samples six sets of plate cultures were prepared in the course of fourteen days, and from the data thus afforded the following Tables are compiled:—

---

* From the *British Medical Journal*, June 17, 1893.

A, *with Infusoria.*

July 19. 3,000,000 Bacteria per c.c.

| | A$_1$ with Air. | A$_2$ without Air. |
|---|---|---|
| July 21.. .. | 215,000 | 567,000? |
| „ 23.. .. | 101,250 | 196,000 |
| „ 25.. .. | 35,552 | 58,000 |
| „ 28.. .. | 42,920 | 97,000 |
| Aug. 1 .. .. | 13,200 | Not connted. |

B, *without Infusoria.*

July 19. 700 Bacteria per c.c.

| | B$_1$ with Air. | B$_2$ without Air. |
|---|---|---|
| July 21.. .. | 1,470,000 | 354,900 |
| „ 23.. .. | 1,285,000 | 797,550? |
| „ 25.. .. | 504,000 | 228,159 |
| „ 27.. .. | 250,500 | 80,800 |
| Aug. 1 .. .. | 121,500 | Not counted. |

Examining this Table, we find there is very little difference in the proportional decrease of bacteria, whether sterilised air be driven through the fluid or not.

Secondly, in this series some very interesting ocular evidence of the purification that was going on was noticed—namely, the water in the A bottles became quite bright and clear, while the water in the B bottles became thicker and more turbid. Prof. von Pettenkofer, to whom I showed these bottles, was particularly struck by this point.

Thirdly, in this last series the presence of Infusoria seemed to have a more marked effect than in the foregoing experiments. For, in ten days, a water containing 3,000,000 bacteria per c.c. decreased in bacterial contents to a little over 13,000, while the water containing no Infusoria not only gave no decrease in numbers, but rose in bacterial contents from 700 per c.c. to 121,500 in the same time, namely ten days.

From all of these experiments it would seem that Infusoria have some powerful influence in the getting rid of bacteria, and, possibly, so aiding in the "self-purification" of water.

# PROCEEDINGS OF SOCIETIES.

## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, Monday, July 3, 1893.*

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—His Royal Highness The Duke of Connaught, K.G. (Honorary Member), and Alfred Walter Soward, F.C.S.

The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—Ludwig Mond, £500; Robert Hannah, £50; Sir Walter Gilbey, Bart., £21; Henry Arthur Blyth, £21; James Blyth, £21.

The special thanks of the Members were returned to Mr. William Schooling for his present of portraits of Sir George B. Airy, Professor J. Crouch Adams, Professor Cayley, and Dr. William Huggins.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

**A Burette Float.**—R. Benedikt (*Chemiker Zeitung*).—The mark is inside, so that it cannot be obliterated by use.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvi., No. 26, June 26, 1893.

**Formation of Natural Aluminium and Iron Phosphates. Phenomena of Fossilisation.** — Armand Gautier.—Ammonium phosphate has its origin in the bacterian decomposition and the oxidation of nitrogenous matter, animal or vegetable, or it may be originally derived from the phosphorus of the igneous rocks and from the ammonia derived from the reactions of the elements of the central nucleus. This ammonium phosphate, as soon as it is dissolved in water, attacks the oxides and the carbonates which it encounters. Thus there are formed not merely the calcium phosphates of the phosphates, but the aluminium, copper, and iron phosphates. Thus minervite, $P_2O_5,Al_2O_3,7H_2O$, is produced by the action of a layer of guano upon a subjacent stratum of hydrargillite. The same reaction gives rise to the mixed aluminium and calcium phosphates found in the small islands of Alta Vela, Redonda, and Commandeur. The author has reproduced these reactions experimentally. In contact with ferrous carbonate dissolved in water containing carbonic acid or of siderose in fine powder, ammonium phosphate produces ferrous phosphate, though very slowly. This is one of the sources of vivianite and of dufrenite. The simultaneous formation of ammonia, hydrogen sulphide, and other products of slow bacterian fermentation, with the intervention of the air dissolved in the waters generally, involves the simultaneous formation—in soils at once calcareous and ferruginous—of calcium phosphates and of pyrites. These substances accompany each other, as in the green-sand of the pas de Calais and the Ardennes, where beds and nodules of phosphates are enclosed among strata rich in pyrites.

**Combinations of Oxalic Acid with Titanic and Stannic Acids.**—E. Péchard.—Oxalic acid yields with mineral acids, such as the titanic and stannic, definite compounds. The author has previously demonstrated this property for molybdic acid, and Rosenheim has pointed it out for tungstic and vanadic acids. In the salts studied there are always 2 mols. of oxalic acid to 1 mol. of titanic acid.

**Researches on the Arsenic and Antimony Chlorosulphides.**—L. Ouvrard.—Dry hydrogen sulphide reacts at common temperatures upon arsenic chloride, giving a yellow precipitate like arsenic sulphide with an abundant escape of hydrochloric acid. The precipitate, when washed with carbon disulphide, has the composition $As_2S_5Cl$. Three antimony chlorosulphides have been already obtained by Cloez and Schneider. The author has obtained the compound $SbS_2Cl$ in reddish brown crystals, and on prolonging the action of the current of hydrogen sulphide there is obtained another compound, $Sb_2S_5Cl$.

**Action of Carbon Monoxide upon Sodammonium and Potassammonium.**—A. Joannis.—The author has obtained with carbon monoxide and potassium a compound potassium carbonyle, $C_2O_2K$. Sodiammonium, $C_2O_2Na$, has a faint lilac tint, and detonates in presence of small quantities of air or water. The temperature of 90° occasions an explosion.

**Combinations of Boron Bromide with Phosphorus Bromides.**—M. Tarible.—Boron bromide combines easily with the two phosphorus bromides, forming the compounds $PBr_3BBr_3$ and $PBr_5,BBr_3$. Both these substances are well crystallised, and are decomposed in the cold by water, chlorine, and gaseous ammonia.

**Action of Zinc and Magnesium upon Metallic Solutions, and on the Determination of Potassa.**—A. Villiers and Fr. Borg.—This paper will be inserted in full.

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### *Bulletin de la Société Chimique de Paris.*
### Series 3, Vols. ix. and x., No. 10.

**Thio-derivatives of Cellulose.**—C. F. Cross, E. J. Bevan, and C. Beadle.—The substance of this paper has already appeared in an English organ.

**Qualitative and Quantitative Analysis of Formaldehyd.**—A Trillat.

**Electric Crucible.**—MM. Ducretet and Le Jeune.—Already noticed.

**Different Toxicities of Stereoisomeric Bodies.**—At the meeting of the Société Chimique, April 28th, C. Chabrié expressed the opinion that stereoisomeric bodies may have different toxicities. He reserved the question of the two conicines, and had studied the four tartaric acids. He showed that the lævo-rotatory acid was more poisonous than the dextro-rotatory acid, both being more poisonous than racemic acid, and the inactive acid incapable of being split up. He represented the relative portions of these acids required to produce a fatal effect as 34·26, 104·24, 165·25, and 196·27. He concludes with the consideration that the spores of Penicillium, mixed with a solution of racemic acid, split it up into dextrorotatory acid, which they destroy, and into a lævo-rotatory acid, which they tolerate for a time. Hence it results that a slightly poisonous solution has become more poisonous under the influence of micro-organisms without the production of a chemical compound of a new species. This will be poisoning without a poison. If, instead of a racemic solution, we have a solution of the inactive acid which cannot be split up, the spores have not increased its toxicity; and the author asks if the intangible differences between an individual enjoying immunity against certain pathogenic microbia and another individual which does not possess this immunity, may not depend on the circumstance that the one has in its liquids the same products as the other, but in a different stereoisomeric condition. The author purposes to study pathological bloods and those of vaccinated and non-vaccinated subjects to verify this hypothesis.

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### *Zeitschrift fur Analytische Chemie.*
### Vol. xxxii., Part 2.

**Detection of Ammonia by the Nessler Reaction.**—L. L. de Koninck.—An alcoholic solution of ammonia gives no yellowish brown precipitate, nor even a colouration, with the Nessler test. Alcohol does not, however, prevent the reaction of ammonia with mercuric chloride (Bohlig's reaction).

**Systematic Method for the Detection and Separation of the more common Acids.**—F. Harrison.—From the Chemical News.

**Micro-chemical Analysis of Rocks.**—Frey (*Pharm. Schweir. Wochenschrift*).—Already inserted.

**Various Applicability of the Centrifugal Machine for Analytical Purposes.**—Various machines have been described by W. Thörner (*Chemiker Zeitung*), C. G. Haubold, F. Heynemann, and Fr. Hugershof (trade circulars).

**Prevention of Bumping in Boiling Liquids.**—G. Craig (Chemical News); also Pellagio, Winkelhofer, and H. Müller in former issues of the *Zeit. Anal. Chemie.*

**Production of the Sodium Light.**—H. Kràl (*Chem. Zeitung*).—Already inserted.

**New Rings for Retort-stands, &c.**—Morris and Hicks.—From the *Chemist and Druggist.*

**Arrangement for Decantation and Filtration.**—W. Saulmann (*Zeit. f. Angew. Chemie*).—This article requires the accompanying figure.

**A New Colorimeter.**—Gallenkamp (*Chem. Zeitung*).—The apparatus consists of two troughs of mirror-glass placed side by side. One of the troughs has the form of a parallelepipedon and contains the liquid in question. The other, which is wedge-shaped downwards, contains the normal solution.

**Laboratory Heating Appliances.**—Various spirit-lamps are described by Barthel (*Chemiker Zeitung*), Muencke (*Ibid.*), and a furnace for organic combustions designed by F. Fuchs (*Zeit. fur Angewandte Chemie*).

**Universal Economical Gas-burner.**—R. Röher (*Chemiker Zeitung*).—*A safety burner* is proposed by Porges. (From a trade circular).

**Laboratory Apparatus for Speedily Heating Liquids.**—Wiesneg.—From the *Journal des Usines a Gaz* and the *Chemiker Zeitung.*

**Preservation of Solutions of Metaphenylendiamine for the Detection of Nitriles and Hydrogen Peroxide.**—G. Denigès (*Journ. de Pharmacie et de Chemie*).—The author dissolves 2 grms of the hydrochloric substance in 100 c.c. of ammonia and places the solution in a bottle fitted with a ground glass stopper. To this solution he adds 5 grms. pulverised animal charcoal, shakes up vigorously several times, allows it to settle, repeats the shaking hourly three or four times, and allows the liquid to subside over night. If the supernatant liquid is not sufficiently decolourised, the shaking must be repeated. In this manner there may be obtained a liquid almost entirely colourless. It keeps for an indefinite length of time in contact with animal charcoal if not more than from 2 to 4 parts of metaphenylendiamine have been used with 100 parts of ammonia. Aqueous and alcoholic solutions cannot be preserved. For detecting nitrous acid 5 drops of the reagent are mixed with 5 c.c. of dilute sulphuric acid (1 : 5). To this mixture, which should be colourless, the author adds 100 c.c. of the water under examination, and heats for five minutes in the water-bath. A yellow colouration, which appears distinct if seen in the direction of the axis of the test-glass, indicates nitrous acid.

**Determination and Separation of the Xylols.**—J. M. Crafts.—From the *Comptes Rendus.*

**Examination of, and Judicial Decision upon, Animal Matter designed for Human Food.**—W. Eber.—From a work published by the author, and already inserted.

**Detection of Extracted Tea used as a Sophisticant.**—W. A. Tichomeirow.—Already inserted.

**Two Air-baths for Heating Substances in Glass Tubes under Pressure.**—H. Pemberton and D. Woodman.—From the *American Chemical Journal* and the *Jour. Soc. Chem. Industry.*

**A Thermometer of Precision.**—Porges.—From a circular.

**Sources of Error in Analyses Owing to the Use of Gas.**—E. von Meyer (*Journal fur Prakt. Chemie*), Van Leeuwen (*Trav. Chim. des Pays-Bas* and *Chem. Zeitung*), Ad. Nieben (*Akad. der Wiesensch in Wien*), Privoznik (*Berichte*), U. Collan (*Chemiker Zeitung*).

**Presence of Lead in Commercial Ammonia said to be pure.**—W. F. Lowe (*Journal Soc. Chem. Industry*).

**Determination of Vanadic Acid.**—A. Ditte (*Comptes Rendus*).

**Reactions of the three Isomeric Amidobenzoic Acids.**—Oechsner de Coninck.—Noticed under *Comptes Rendus.*

**Detection of Phenoles.**—L. M. A. Lambert (*l'Union Pharmacetique.*—Already inserted.

**Detection of Nitrobenzene.**—J. Marpurgo (*Pharm. Post*).—Already inserted.

**Determination of Nitrogen in Organic Substances.**—Notices of papers by Association of Official Agricultural Chemists (Chemical News), E. B. Voorhees (*Ibid.*), J. H. Smith (*Chemiker Zeitung*), J. O'Sullivan (*Journal Soc. Chem. Industry*), Frankland (*Phil. Trans.*), Keating Stock (*Analyst*), Hugnet (*Journal de Pharmacie* and *Chemiker Zeitung*), Vincent Edwards (Chemical News), H. Synder (*Jour. Amer. Chem. Soc.*), E. Fricke (*Zeit. Angewandte Chemie*), Stutzer (*Zeit. Ang. Chemie*), Ulsch (*Chem. Centralblatt*), Boyer (*Comptes Rendus*), Arnold and Wedemeyer (*Amer. Journ. Pharmacy*).

**Determination of Vanilline.**—F. X. Moerk (*American Journal of Pharmacy*).—The author has previously shown that factitious vanilline, on treatment with bromine-water and addition of ferrous sulphate, takes a bluish green colour. He now finds that natural vanilla extract, if previously purified with recently precipitated lead hydroxide, gives the same reaction.

**Gottlieb's Modification of Röse's Method of Determining Milk Fat.**

**Examination of Olive Oil and of Butter.**—Roaul Brulte.—From the *Comptes Rendus*.

**Execution of the Reaction for Sesame Oil.**—G. Ambübl (*Schweiz. Wochen. f. Pharm.*).—The author dissolves 0·1 to 0·2 grm. of white sugar in 20 c.c. hydrochloric acid of sp. gr. 1·18, adds 10 c.c. of the oil, and shakes it well up. Sesame gives an intense red colour. Olive oil, containing only 10 per cent of oil of sesame, gives a pure deep rose colour. Pure olive oil (Tuscan, San Remo, Nice, and Provence) gives no red colour, only the Bari oils after some minutes turn a more violet-blue shade. Old, very rancid sesame oil gave an indigo-blue colour.

**New Normal Hydrometer for Must.**—Barth (*Weinlauebe*).—The author states the degrees of the must of different grapes in degrees of Oechsle's scale.

**Agreements on the Analysis of Malt.**—(*Dingler's Polytech. Journal*).

**Lavender Oil and Bergamot Oil.**—J. Bertram and H. Waldbaum.—The editors refer to a commercial report by Schimmel and Co.

**Determination of Quinine in Cinchona Barks.**—J. H. Schmidt.

**Micro-chemical Distinction of Alkaloids and Protein Substances.**—Errera.—From the *Pharm. Journal* and *Transactions*.

**Valuation of Ipecacuanha.**—G. Kottmeyer (*Pharm. Post*).—Already inserted.

**Micro-chemical Detection of Phosphorus in the Tissues.**—L. Lilienfeld and A. Monti (*Zeit. f. Physiol. Chemie*).

**Determination of Uric Acid.**—F. G. Hopkins.—From "Guy's Hospital Reports."

**Action of Benzoyl Chloride upon Ammonia, Urea, and Kreatinin.**—V. Lehmann (*Zeit. Physiol. Chemie*).—No deposition of benzamid is observed on treating human urine with benzoyl, though it is obtained from the urine of some of the lower animals. Further papers on the detection of sugar in urine, on that of the carbohydrates in general in urine and in the blood, are not adapted for useful abstraction.

**Determination of Glycogen in the Liver and the Muscles.**—S. Fränkel (*Pfluger's Archiv*).—The author simplifies the ordinary process by using trichloracetic acid instead of mercury-potassium iodide for the precipitation of the albumenoids.

**Identification of Coniin in a Toxicological Case.**—Launcelot W. Andrews.—From the *American Chemical Journal*.

**Researches on Cobalt.**—Hugo Remmler (*Zeit. fur Anorganische Chemie*).—Already inserted.

## MISCELLANEOUS.

**The New Heidelberg Laboratory.**—We perceive that in the new chemical laboratory of the University of Heidelberg a special room is set apart for chemico-legal investigation.

**Quantitative Detection of Bacteria.**—Dr. Gottstein proposes the use of hydrogen peroxide for recognising the presence of bacteria. If the number of bacteria in a specimen of water reaches 10,000 per c.c., there is a brisk evolution of oxygen, and there is an appreciable liberation of this gas even with 1000 per c.c.

**Owens College, Manchester.**—Bishop Berkeley Research Fellowships have been awarded by the Council as follows:—H. B. Pollard, M.A. (Oxon), in Zoology; Albert Griffiths, M.Sc. (Vict.), and J. A. Harker, D.Sc. (Tübingen), in Physics; Bevan Lean, B.A., B.Sc. (Lond.), in Chemistry; and a Fellowship has been renewed to Stanley Dunkerley, M.Sc. (Vict.), in Engineering.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

C. S. will be glad to know of the best *small* book on the analysis of steel and iron, and the analysis of ores, in English or French.

THE CHEMICAL NEWS.

VOL. LXVII., No. 1757.

## ON THE RATIO OF THE SPECIFIC HEATS OF THE PARAFFINS AND THEIR MONOHALOGEN DERIVATIVES.*

By J. W. CAPSTICK, M.Sc. (Vict), B.A. (Camb.),
Scholar and Coutts-Trotter Student of Trinity College, Cambridge.

THE experiments were undertaken to find whether the internal energy of the molecules of organic gases, as deduced from the ratio of the specific heats, showed any regularities corresponding to the chemical resemblances symbolised by the graphic formulæ.

The paraffins and their monohalogen derivatives are very suitable for the purpose, as their chemical relations to each other are simple, they are easily volatile, and are stable enough to be unaffected by ordinary purifying agents.

For the ratio of the specific heats we can calculate the relative rates of increase of the internal energy and the energy of translation of the molecules per degree rise of temperature, and, the aim of the experiments being to compare the rates of increase of the internal energy of different gases, it was decided to keep the translational energy constant by working at a constant temperature. Consequently the determinations were all made at the temperature of the room.

The ratio of the specific heats was calculated from the velocity of sound in the gases. This was determined by Kundt's method, using a double-ended form of apparatus, in all essential features the same as that described in *Pogg. Ann.*, vol. cxxxv. The tube in which the dust figures were made was 125 c.m. long and 26 m.m. in diameter, which Kundt showed to be great enough to avoid any lowering of the velocity of sound from the influence of the walls of the tube.

Lycopodium was used for forming the figures in the hydrocarbons and in methyl and ethyl chlorides, but in the heavier gases it became sticky, and would not move readily, so for these silica was used.

To measure the figures a piece of apparatus was constructed, consisting of a pair of parallel platinum wires, carried by a framework which slides along a steel slide graduated to millimetres. The tube was placed on V-shaped supports, parallel to the scale, and between the wires, which were so adjusted that their plane passed through the centre of the nodes. The position of the framework was then read on the scale, tenths of a millimetre being estimated with the help of a lens. With figures of average quality the setting of the wires could be repeated so as to agree within two or three tenths of a millimetre. The greatest divergence of the observed length of any one figure from the mean of the series was usually about five or six tenths of a millimetre.

The calculation of the ratio of the specific heats from the velocity of sound requires the density of the gas to be known, a circumstance which makes the method very sensitive to small amounts of impurity in the material.

Regnault's value was used for methane, and every precaution was taken to secure pure gas. Two methods of preparation were used, Gladstone and Tribe's, by the action of the copper-zinc couple on methyl iodide and alcohol, and Frankland's, by the action of zinc methyl on water. After each experiment an analysis of the gas was made to test its purity and to determine the amount of air present, for which a correction was made.

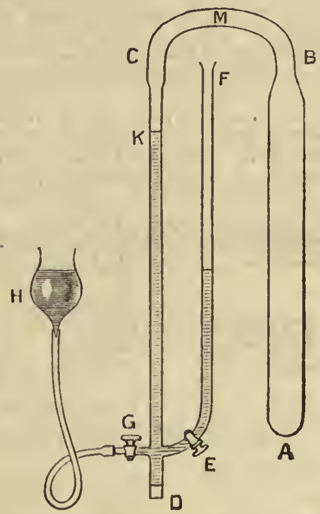
The ethane was prepared by the action of zinc ethyl on water, and for it the theoretical density calculated from the molecular weight was used.

For the preparation of propane, isopropyl iodide was reduced by zinc and hydrochloric acid, and the gas was freed from air by liquefaction in a freezing mixture of ether and solid carbonic acid, after passing through fuming sulphuric acid and potash, and over 30 grms. of palladium.

Methyl and ethyl chlorides were prepared in the usual way, by passing hydrochloric acid into a boiling solution of zinc chloride in the corresponding alcohol, and purified by re-distillation through suitable reagents. All the rest of the compounds were purchased from Kahlbaum, and were dried and fractionated before being used.

The vapour densities of propane and all the halogen compounds were determined at various pressures for the material, as it was used in the velocity of sound experiment, thus avoiding to a great extent any error arising from impurity.

The apparatus used for this purpose is shown in figure. Before joining the parts together, the tube, C D, is calibrated, and after it has been attached, but before the side tubes are fixed on, the volume of the whole is determined by filling with water and weighing. Then, from the calibration of C D, the volume is known between A and a file mark at K.



A weighed quantity of the liquefied gas whose vapour density is required is sealed up in a small tube with capillary ends, and introduced at D, and, by inclining the apparatus, is made to slide over the bend and rest at M. The end, D, is then closed with a cork, and the apparatus exhausted through the three-way tap, G; on the completion of which operation mercury is allowed to flow in from the reservoir, H, and the tap, E, is opened. The difference of the levels of the mercury in the two tubes is read with a cathetometer, and, subtracted from the height of the barometer, gives the pressure of the residual air. On tilting the apparatus, the tube slides over into the wider part, and the end breaks off, allowing the liquid to evaporate. By reading the levels again we get the pressure of the gas, and knowing its weight and volume, we have all the materials required for calculating its specific gravity.

In the experiments the reservoir was always adjusted so that the level of the mercury in C D stood near the mark at K, thus simplifying the calculations a little.

The apparatus was found to give values of the vapour density concordant to about 1 part in 1000.

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* Abstract of a Paper read before the Royal Society, June 15, 1893.

The formula used in calculating the ratio of the specific heats was—

$$\gamma = 1{\cdot}408 \times \rho \times \left(\frac{l}{l'}\right)^2 \left(1 + \frac{1}{p}\frac{d}{dv}(pv)\right),$$

the last factor being added to the ordinary formula to correct for the divergence of the gas from Boyle's law.

The correction is obtained at once by putting in the equation—

$u^2 = -\gamma v^2 \left(\frac{dp}{dv}\right)_t$ the value of $\left(\frac{dp}{dv}\right)_t$ given by

$$\left(\frac{dpv}{dv}\right)_t = p + v\left(\frac{dp}{dv}\right)_t.$$

From the vapour-density determinations a curve is constructed giving $pv$ in terms of $v$, and the slope of this curve at any point gives the value of $\frac{d}{dv}(pv)$ in arbitrary units. Dividing by the corresponding value of $p$ in the same units, we obtain the amount of the correction.

The correction increases the ratio of the specific heats by from 1 to 2 per cent in most cases.

Observations varying in number from three to nine were made on each gas, the extreme range of the values being 2 per cent for marsh gas, 1½ per cent for methyl iodide, and 1 per cent, or less, for the rest.

The mean values are shown in the following table:—

| | | |
|---|---|---|
| Methane | $CH_4$ | 1·313 |
| Methyl chloride | $CH_3Cl$ | 1·279 |
| Methyl bromide | $CH_3Br$ | 1·274 |
| Methyl Iodide | $CH_3I$ | 1·286 |
| Ethane | $C_2H_6$ | 1·182 |
| Ethyl chloride | $C_2H_5Cl$ | 1·187 |
| Ethyl bromide | $C_2H_5Br$ | 1·188 |
| Propane | $C_3H_8$ | 1·130 |
| Normal propyl chloride | $nC_3H_7Cl$ | 1·126 |
| Isopropyl chloride | $iC_3H_7Cl$ | 1·127 |
| Isopropyl bromide | $iC_3H_7Br$ | 1·131 |

From this Table we have the interesting result that the gases fall into four groups, the members of any one group having within the limits of experimental error the same ratio of the specific heats.

These groups are—

I.—Methane.
II.—The three methyl compounds.
III.—Ethane and its derivatives.
IV.—Propane and its derivatives.

If the members of a group have the same ratio of the specific heats, we know, from a well-known equation in the kinetic theory of gases, that the ratio of the internal energy absorbed by the molecule to the total energy absorbed, per degree rise of temperature, is the same for all. Hence we have the result that, with the single exception of marsh gas, the compounds with similar formulæ have the same energy-absorbing power, a result which supplies a link of a kind much needed to connect the graphic formula of a gas with the dynamical properties of its molecules.

From the conclusion we have reached it follows with a high degree of probability that the atoms which can be interchanged without effect on the ratio of the specific heats have themselves the same energy-absorbing power, their mass and other special peculiarities being of no consequence. Further, the anomalous behaviour of methane confirms what was clear from previous determinations, namely, that the number of atoms in the molecule is not in itself sufficient to fix the distribution of energy, and suggests that perhaps the configuration is the sole determining cause.

If this is so, it follows that ethane and propane have the same configuration as their monohalogen derivatives, but that methane differs from the methyl compounds, a conclusion that in no way conflicts with the symmetry of the graphic formulæ of methane and its derivatives, for this is a symmetry of reactions, not of form.

## ON THE IODOMETRIC DETERMINATION OF THE NITRATES.*

By HIPPOLYTE GRUENER.

Dr. Koninck and Nihoul (*Zeitschr. f. Angewandte Chem.*, 1890, p. 477) describe a method for the iodometric determination of nitrates, in which the decomposition of the nitrates is effected by the action of gaseous hydrochloric acid, the gases evolved being passed into potassium iodide; but the method is a cumbersome one. In a former paper (*Amer. Journ. Sci.*, xliv., p. 117), by Prof. Gooch and myself, a method was described according to which nitrates were decomposed successfully and easily by a solution of manganous chloride in hydrochloric acid, the products of decomposition being passed into potassium iodide, and the liberated iodine titrated with sodium thiosulphate. The ease with which hydriodic acid has been applied in this laboratory as a reducing agent in the determination of arsenic, chloric, and antimonic acids (*Amer. Journ. Sci.*, xl., p. 66; xlii., p. 220; xlii., p. 213) has suggested its application for the same end to nitric acid, and the present paper is the account of attempts in this direction.

*The Action of Phosphoric Acid and Potassium Iodide upon Nitrates.*—The decomposition of the last traces of nitrates in presence of potassium iodide and sulphuric acid does not occur except at very great concentrations. and, as at great concentrations sulphuric acid in presence of hydriodic acid itself liberates iodine, the use of syrupy phosphoric acid to bring about the required decomposition naturally suggested itself. Various attempts to simplify the process while still registering the amount of reduction by arsenic acid in the residue proved futile, and a distilling apparatus was found to be necessary. For this purpose a small retort was used, the neck of which was bent downward about 2 inches from the body, so that the retort itself might be tipped backward, allowing the unbent portion of the retort to run upward, thus guarding against loss from spattering. Into the tubulature of the retort was ground a glass tube drawn out at both ends to serve as a perforated stopper for the entrance of carbon dioxide. The neck was passed through a rubber stopper into a side-neck Erlenmeyer flask, the exit tube of which was prolonged and dropped into a side-neck test-tube used as a trap. The retort was covered with a simply contrived hood which kept the upper parts warm and prevented the iodine from settling anywhere. In the retort was placed the nitrate with an excess of potassium iodide, and in the receiver a known a known amount of decinormal solution of arsenious oxide strongly alkaline with hydrogen sodium carbonate and diluted to a convenient bulk. The trap contained nothing but water. The phosphoric acid used was at first 10 c.m.³ of strong acid, sp. gr. 1·7, with varying amounts of water; but when it was found that the amount of water present was an essential feature, a definite mixture was used as designated in the Tables. The acid was added to the retort last of all, and after carbon dioxide had been passed for a sufficient length of time heat was applied. The carbon dioxide was evolved in a Bonn generator from materials which had been carefully boiled, and cuprous chloride was added to the acid in the generator to take up the oxygen from any traces of air. Between the introduction

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* *American Journal of Science*, xlvi., July, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

of phosphoric acid into the retort and the application of heat a good stream of gas was passed for ten minutes, at the end of which time the bubbles escaping at the last trap were completely absorbed in potassium hydrate of the requisite strength.

The first experiments were in blank with no nitrate present. Upon warming the mixture of phosphoric acid and 2 grms. of the iodide, signs of free iodine were developed; and by titration of the contents of the receiver at the end, iodine to the amount of 0·0014 grm. was found to have been liberated, either by residual traces of air or by dissociation. The experiment was repeated; but in this case all the water used had been boiled immediately before the experiment, and here iodine to the extent of 0·0009 grm. only was found to have been liberated. The cause and remedy for this liberation of iodine are discussed presently. A series of experiments was performed to study the action of the reagents when nitrates were present.

The method of procedure was as follows:—The nitrate was taken for convenience from a solution of 5 grms. in 500 c.m.³ of water. The iodide was introduced dry or in solution, according to the bulk of water allowable. This mixture was boiled a moment to drive out all air, the phosphoric acid was then added, and carbon dioxide was passed as described, the receiver containing the arsenious oxide and the trap being already in position. It had been found that all but a trace of iodine was caught in the first receiver, so that the rubber stopper closing it could do no harm. When large amounts of nitrate were used, the clots of solid iodine settling out in the receiver were dissolved by means of a crystal or two of potassium iodide. The solution in the retort was boiled until it was clear that all the iodine had distilled over, and usually until the boiling in the retort had ceased. It was found advisable to empty the retort so soon as it was cool enough, else the phosphoric acid became unmanageable. The retort after each experiment was washed out with ammonia and water.

The results of these first experiments are shown in Table I.

Table I.

| | $KNO_3$ taken. | KI taken. | Water added to 10 c.m.³ of phosph. acid, sp. gr. 1·7. | $KNO_3$ found. | Error in $KNO_3$. | Error in $HNO_3$. |
|---|---|---|---|---|---|---|
| Series 1. | | | | | | |
| | Grm. | Grm. | C.m.³. | Grm. | Grm. | Grm. |
| 1 | 0·0005 | 0·2 | 2 | 0·0009 | 0·0004+ | 0·0002+ |
| 2 | 0·0010 | 0·2 | 2 | 0·0012 | 0·0002+ | 0·0001+ |
| 3 | 0·0020 | 0·2 | 2 | 0·0021 | 0·0001+ | 0·0001+ |
| 4 | 0·0050 | 0·2 | 2 | 0·0055 | 0·0005+ | 0·0003+ |
| 5 | 0·0100 | 0·2 | 2 | 0·0093 | 0·0007− | 0·0004− |
| 6 | 0·0100 | 0·2 | 2 | 0·0103 | 0·0003+ | 0·0002+ |
| 7 | 0·0200 | 0·3 | 3 | 0·0216 | 0·0016+ | 0·0010+ |
| 8 | 0·0200 | 0·3 | 3 | 0·0192 | 0·0008− | 0·0005− |
| 9 | 0·0200 | 0·3 | 3 | 0·0205 | 0·0005+ | 0·0003+ |
| 10 | 0·0200 | 0·3 | 3 | 0·0205 | 0·0005+ | 0·0003+ |
| 11 | 0·0500 | 0·5 | 6 | 0·0496 | 0·0004− | 0·0002− |
| 12 | 0·0500 | 0·5 | 6 | 0·0499 | 0·0001− | 0·0001− |
| 13 | 0·0300 | 0·5 | 4 | 0·0293 | 0·0007− | 0·0004− |
| Series 2. | | | | | | |
| 14 | 0·0616 | 1·5 | 1 | 0·0682 | 0·0066+ | 0·0039+ |
| 15 | 0·0570 | 2·5 | 1 | 0·0643 | 0·0073+ | 0·0045+ |
| 16 | 0·1030 | 1·1 | 1 | 0·1061 | 0·0031+ | 0·0018+ |
| 17 | 0·1062 | 1·1 | 1 | 0·1197 | 0·0135+ | 0·0081+ |

With one or two exceptions the results of Series 1 are fairly good. Those of Series 2 are very bad. The only essential difference between the two series is in the dilution of the phosphoric acid used. In the first series there is always enough water present to make the specific gravity of the phosphoric acid no higher than 1·6 for small amounts of iodide and nitrate, and lower than that number when these amounts are increased. The suggestion is obvious that dissociation of the hydriodic acid may occur at the boiling-point of the stronger acid. According to Berthelot (*Ann. de Chim. et Phys.* [IV.], xx., p. 392) aqueous solutions of hydriodic acid under pressure begin to dissociate at 275°, or even under. The temperature of the retort at the end of an experiment was taken and found to be far beyond the range of a thermometer reading to 360°. It is evident, then, that under the conditions there should be opportunity for dissociation. Four experiments in which potassium iodide was treated with phosphoric acid, sp. gr. 1·7, undiluted, gave of liberated iodine caught in arsenious acid 0·0030 grm., 0·0044 grm., 0·0049 grm., 0·0030 grm. of iodine, corresponding to 0·0008 grm., 0·0012 grm., 0·0013 grm., 0·0008 grm. of potassium nitrate respectively. These results would account only in part for the errors noted, but they are in the same direction. Chapman (*Journ. Chem. Soc.*, xx., 1867, p. 166) has found that concentrated hydriodic acid acting upon organic nitrates and nitrites reduces them not alone to nitric oxide, but even in part to ammonia. The conditions of the experiments in Series 2 approximate to concentration of the hydriodic acid, and the reaction that Chapman found probably takes place here to a limited extent. Concentration of the hydriodic acid then must be avoided, both to eliminate dissociation and excessive reduction of the nitrate.

Therefore the plan was adopted of diluting the solution, so that the temperature and concentration should be effective in decomposing the nitrate, but should not bring about the complications just mentioned. A blank experiment made thus, 18 c.m.³ of a solution of phosphoric acid of specific gravity 1·39, being used, gave of liberated iodine only 0·0004 grm. corresponding to 0·0001 grm. of potassium nitrate. So that under these conditions we may be assured that dissociation occurs, if at all, to only a slight extent. In the following experiments, therefore, the nitrate is decomposed in presence of dilute phosphoric acid, the dilution and the quantity taken being included in Table II.

Table II.

| | $KNO_3$ taken. Grm. | KI taken. Grm. | Found. Grm. | Sp. gr. of solution of phosphoric acid. | Amount of sol. used. C.m.³. | Error $KNO_3$. Grm. | Error $HNO_3$. Grm. |
|---|---|---|---|---|---|---|---|
| Series 3. | | | | | | | |
| 18 | 0·0500 | 1 | 0·0500 | 1·43 | 17 | 0·0000 | 0·0000 |
| 19 | 0·0200 | 0·5 | 0·0201 | 1·43 | 17 | 0·0001+ | 0·0001+ |
| 20 | 0·0200 | 1 | 0·0198 | 1·43 | 17 | 0·0002− | 0·0001− |
| 21 | 0·0250 | 1 | 0·0250 | 1·43 | 17 | 0·0000 | 0·0000 |
| 22 | 0·0300 | 1 | 0·0307 | 1·43 | 17 | 0·0007+ | 0·0004+ |
| 23 | 0·0300 | 1 | 0·0312 | 1·43 | 17 | 0·0012+ | 0·0007+ |
| 24 | 0·0350 | 1 | 0·0353 | 1·43 | 17 | 0·0003+ | 0·0002+ |
| 25 | 0·0400 | 1 | 0·0409 | 1·35 | 20 | 0·0009+ | 0·0006+ |
| 26 | 0·0450 | 1 | 0·0444 | 1·35 | 20 | 0·0006− | 0·0004− |
| 27 | 0·0500 | 1 | 0·0499 | 1·37 | 20 | 0·0001− | 0·0001− |
| Series 4. | | | | | | | |
| 28 | 0·0600 | 1 | 0·0568 | 1·37 | 20 | 0·0032− | |
| 29 | 0·0600 | 1 | 0·0575 | 1·37 | 20 | 0·0025− | |
| 30 | 0·0600 | 1 | 0·0576 | 1·37 | 20 | 0·0024− | |
| 31 | 0·0600 | 2 | 0·0588 | 1·37 | 20 | 0·0012− | |
| 32 | 0·0600 | 2 | 0·0605 | 1·37 | 18 | 0·0005+ | |
| 33 | 0·0700 | 2 | 0·0708 | 1·37 | 18 | 0·0008+ | |
| 34 | 0·0800 | 2 | 0·0811 | 1·37 | 18 | 0·0011+ | |
| 35 | 0·0900 | 2 | 0·0842 | 1·37 | 18 | 0·0058− | |
| 36 | 0·1000 | 2 | 0·0996 | 1·37 | 18 | 0·0004− | |
| 37 | 0·1000 | 2 | 0·1012 | 1·37 | 18 | 0·0012+ | |
| 38 | 0·1000 | 1·5 | 0·0909 | 1·37 | 18 | 0·0091− | |
| 39 | 0·1000 | 2·5 | 0·0979 | 1·37 | 18 | 0·0021− | |
| 40 | 0·1021 | 3 | 0·1005 | 1·43 | 17 | 0·0016− | |
| 41 | 0·1032 | 2 | 0·0949 | 1·43 | 17 | 0·0085− | |

The iodine of 41 was collected in potassium iodide and titrated with thiosulphate. Series 3 requires little special comment. The experiments ran along smoothly, the manipulation was easy, the care required in watching very little, and the results are fairly satisfactory. The causes leading to the high results of Series 2 seem entirely eliminated by the dilution. Series 4 is a direct continuation of Series 3, differing in the single point that larger amounts of nitrate are handled. These results with some exceptions are decidedly low. It appears that with a fair percentage of water present, as the amounts of nitrate grew larger, the error became a negative one. The explanation for this seemed to be that the last portions of nitric acid must have distilled before decomposition, whenever the original amount was large. Nitric acid was accordingly tested for in the distillate, and to this end all the conditions of the experiment were repeated, except that the receiver contained only water. Of the nitrate 0·4 grm., and of the iodide 4 grms., twice the amount theoretically necessary, were put into the retort, and at the end of the experiment the solution in the receiver was boiled with hydrogen peroxide to decompose the hydriodic acid and drive out the iodine, care being taken to keep enough water to hold any nitric acid present. When all the iodine was gone sodium carbonate was added, the solution evaporated, and the residue ignited and tested with a saturated solution of manganous chloride in hydrochloric acid, as described in the previous paper above mentioned. By this means 0·0002 grm. potassium nitrate are very easily detected in 10 c.m.³ of solution. Nitric acid was found in the distillate of this experiment as well as in two others conducted with 0·2 grm. and 0·1 grm. of the nitrate respectively. The residues in the retorts of these three tests showed no trace of nitric acid.

The process seems reliable enough, then, for estimating nitrates in small quantities not exceeding an equivalent of 0·04 grm. or 0·05 grm. of potassium nitrate. Every experiment performed with quantities not larger than 0·05 grm. has been given here, except four in which an imperfection in the apparatus showed an obvious mechanical loss. The errors in these experiments lie between the extremes of 0·0016 grm. + and 0·0008 grm. − on the nitrate, with an average error of 0·00016 grm. If Series 3 alone is taken, in which the dilution of the phosphoric acid was regulated, we have as extreme errors 0·0012 grm. + and 0·0006 grm. −, with a mean error of 0·0002 grm. +. With quantities of nitrate above 0·05 grm. the process does not seem a safe one, inasmuch as with a moderate amount of water present some nitric acid distils over undecomposed, and with little water present other complications as seen above arise.

The method so far as it is applicable may be summed up as follows:—The nitrate not to exceed in amount 0·05 grm. of potassium nitrate, is introduced into a retort, together with ten times its weight of potassium iodide, and 17 to 20 c.m.³ of phosphoric acid, of specific gravity 1·43. All water used should be recently boiled. Carbon dioxide is passed from a receiver carefully set up. The neck of the retort passes into a receiver containing a known amount of decinormal arsenious oxide, alkaline with a good excess of hydrogen sodium carbonate, and diluted to a convenient bulk. To this flask is attached for additional safety a simple trap containing water. The solution in the retort is boiled until it is clear that no more iodine remains, when the receiver, after proper washing and addition of the liquid in the trap, is titrated with iodine to find the amount of arsenious oxide still left. This gives the measure of the iodine evolved and consequently of the nitrate present, according to the equation—

$$2HNO_3+6HI=4H_2O+2NO+3I\text{-}I.$$

(To be continued).

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**Borings at Paruschowitz.**—In May last the borings at Paruschowitz, in Upper Silesia, reached the depth of 2000 metres. Geothermic experiments are being made with very sensitive thermometers..—*Revue Universelle des Mines.*

## CONGRESS OF THE SOCIETY OF GERMAN NATURALISTS AND PHYSICIANS.

This Association, founded by the illustrious Lorenz Oken, will hold its 65th Congress at Nürnberg, from Sept. 11th to 15th inclusive. It is well known that this body was the model on which the British Association and similar societies in France, America, &c., were afterwards formed. The original German body differs, however, in many respects from imitators in other countries. It includes, in addition to the "Naturforscher,"—a term much more comprehensive than its English equivalent "Naturalist,"—the medical practitioners of all grades. This combination would not, we think, prove desirable in Britain, as we have an annual Medical Congress. It is free from the worst defect of the British Association—the so-called Economical and Statistical Section. The Germans know that statistics must be considered not as a science, but merely as a method applicable in various sciences, and that political economy borders perilously upon party politics and finds sufficient scope in Chambers of Commerce.

The German Association is also free from that phenomena of technological considerations by which its French colleague is unfavourably characterised.

The Nürnberg meeting will comprise 32 sections—namely, 1, mathematics and astronomy; 2, physics; 3, chemistry; 4, botany; 5, zoology; 6, entomology; 7, mineralogy and geology; 8, ethnology and anthropology; 9, anatomy; 10, physiology; 11, pathology; 12, pharmacology; 13, pharmacy and pharmacognosia; 14, internal medicine; 15, surgery; 16, obstetrics and gynæcology; 17, medical treatment of children; 18, neurology and psychiatry; 19, medical treatment of the eyes; 20, medical treatment of the ears; 21, laryngology and rhinology; 22, dermatology and syphilis; 23, hygiene and medical police; 24, forensic medicine; 25, medical geography, climatology, tropical hygiene; 26, military sanitation; 27, dentistry; 28, veterinary medicine; 29, agricultural chemistry; 30, instruction in mathematics and natural science; 31, geography; 32, instrumental knowledge.

Men of science who purpose visiting this Congress may learn all further particulars on application to Herrn Medicinalrath Merkel, Nürnberg, Josephsplatz 3, and may engage apartments in hotels or private lodgings through the medium of Herr J. Gallinger, Nürnberg, Burgstrasse 8. Such applications should be made as early as possible, as rooms cannot be guaranteed after August 31st.

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## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 32).

### Part II.

*Table of Sulphates.*

It will be convenient and will save space to preface the Table of Sulphates with the general formula of the *alums*. Omitting the selenates and mixed selenates and sulphates, the general formula is $M_23SO_4.N_2SO_4.24H_2O$; where M = Al, Cr, Mn, Fe, In, or Ga; and N = Na, K, Rb, Cs, $NH_4$, Ag, or Tl.

The best known combinations are—

| M | with N. |
|---|---|
| Al | ,, Na, K, $NH_4$, Rb, Cs, $NH_3(C_2H_5)$, Ag, or Tl. |
| Cr | ,, Na, K, or $NH_4$. |
| Mn | ,, — K or $NH_4$. |
| Fe | ,, — K or $NH_4$. |
| Ga or In | ,, — — $NH_4$. |
| $M_2$ | ,, |
| CrAl | ,, — K or $NH_4$. |

The *alums* are strictly isomorphous. They crystallise in forms belonging to the cubic system, usually in cubes or octahedra, or in octahedra combined with cubes.

| | No. | Neme. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| ALUMINIUM. | | | | | | | |
| $Al_2(SO_4)_3$ .. .. .. .. | 1 | | | | | | |
| $Al_2(SO_4)_3+18H_2O$ .. | 2 | Alunogen. | M | (*a*) In six-sided tablets.<br>(*b*) Radiating tufts like horse tails and grasses. | 1st order. | About 45° from *e*. | Boundaries of platy crystals marked by fine dark lines. |
| *Double Salts.* | | *See alums ante.* | | | | | |
| BARIUM. | | | | | | | |
| $BaSO_4$ .. .. .. .. | 3 | Barytes. | R | (*a*) Modified rhombic and rectangular prisms. | 1st order. | (*a*) $\parallel$ to *e*. | (*b*) Extinguish at 45° from the arms of skeleton. |
| $(BaSr)SO_4$ .. .. .. | 4 | *See Sr.* | | (*b*) X-shaped skeleton crystals resembling ice crystals. | | | |
| BERYLLIUM. | | | | | | | |
| $BeSO_4+4H_2O$ . .. | 5 | | T | (*a*) Prisms with pyramidal terminations.<br>(*b*) In radiating and star-shaped arborescent forms. | 7th order. | (*a*) *R.L.* to *e*.<br>(*b*) $\parallel$ to fibres. | Axial sections in *c.p.l.* cross well seen. Negative. |
| $BeSO_4+7H_2O$ . .. | 6 | — | M | In prisms, sometimes twinned. | 3rd order. | At a high angle to *e* and to twinning plane. | |
| $BeSO_4K_2SO_4+2H_2O$ | 7 | — | — | Globulites either isolated or in perlitic looking base. | 1st order. | In quadrants at *R.L.* to *Q.W.* | |
| CALCIUM. | | | | | | | |
| $CaSO_4$ .. .. .. .. | 8 | Anhydrite. | R | Usually combinations of the prism, pinacoids and basal planes. Microscopic crystals often boat-shaped. | 4th order. In micro-crystals, usually not higher than 2nd order. | $\parallel$ to *e*. | Interference fig. in *c.p.l.* is seen when prism lies on its macropinacoidal face. |
| $CaSO_4+2H_2O$ . .. | 9 | Gypsum. | M | (*a*) Acicular prisms often in radiating groups.<br>(*b*) Swallow-tailed twins.<br>(*c*) Short prisms with rhombic outline. Acute angle about 50°. See Part III. | 1st order. | (*a*) About 38° from *e*, measured in direction of acute angle of rhomb. | Refraction nearly the same as Canada balsam, viz., Gypsum $n=1{\cdot}52$. Balsam $n=1{\cdot}54$. |
| $CaSO_4K_2SO_4+H_2O$ | 10 | Syngenite. | M | Small tabular crystals generally showing 6 or 8 sides in outline. | 1st order. | About 3° from (100). | No. 10. Refraction not far from balsam. |

*Remarks.*

*No.* 2.—Dissolves in two parts of water. The tablets overlap each other and form platy masses, in which six-sided micaceous crystals can be distinguished. Two angles of 92° and four of 134°. When not mounted in Canada balsam the crystals have a peculiar pearly gloss. The pearly appearance is produced by a granular salt white in reflected and opaque in transmitted light, reminding one of the beginning of kaolinisation in felspar. Query, is this one of the basic sulphates $Al_2O(SO_4)_2+H_2O$ or $Al(OH)SO_4$?

*No.* 3.—Almost insoluble in $H_2O$ (soluble 1 in 400,000). The precipitate formed by adding $H_2SO_4$ to an aqueous solution of a Ba salt does not yield definite crystals under the microscope. A Ba salt heated with concentrated $H_2SO_4$ dissolves in part, and deposits on cooling crystals of $H_2SO_4+BaSO_4$. If exposed to moist air, crystals of $H_2SO_4+BaSO_4+2H_2O$ are deposited. See Part III.

*No.* 5.—Beryllium readily forms basic sulphates. They may be obtained by boiling the normal sulphate (No. 5) with beryllium carbonate. They form gelatinous masses. The normal salt dissolves at the ordinary temperature in its own weight of water.

*No.* 6.—Separates out from an acid solution of the normal salt.

*No.* 7.—The outer margins of the globulites are hard black lines. They do not possess a radiate structure. The centres are often white in reflected, and brown and opaque in transmitted, light. The ground-mass may be either glassy or micro-granular.

*No.* 8.—Forms when concentrated $H_2SO_4$ is used. With dilute $H_2SO_4$ No. 9 forms.

*No.* 9.—See Part III.

*No.* 10.—Soluble in water 1 in 400 with separation of some gypsum. Slide shows numerous needles and prisms of gypsum with stumpy crystals of syngenite, roughly speaking resembling augite in habit. Twinning very common. Extinction between twins 15°—24°, sometimes less. Of the natural mineral Dana says it is elongated in the direction of vertical axis, and that the plane (100) always predominates.

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| **Calcium.** | | | | | | | |
| $CaSO_4Na_2SO_4$ .. | 11 | Glauberite. | M | (*a*) Crystals of approximately rhombic outline with a strong rib down centre radiating like the petals of a flower.<br>(*b*) Radiating fibrous groups. | (*a*) Blue of 2nd order.<br>(*b*) Double refraction feeble. | (*a*) At a high angle to rib.<br>(*b*) Sometimes at high sometimes at low angle to fibre. | |
| **Cerium.** | | | | | | | |
| $Ce(SO_4)_2+7H_2O$ .. | 12 | Ceric sulph. | — | Reniform mass. | — | — | — |
| $Ce_2(SO_4)_3$ . .. .. | 13 | Cerous ,, | — | Small crystals and long needle-shaped prisms badly terminated. | — | — | No. 13. Straight extinction. |
| $Ce_2(SO_4)_3+8H_2O$ .. | 14 | ,, ,, | M | Prisms terminated by clinodomes. | 7th order. | At a very high angle to plane of twinning and to *e*. | No. 14. Prisms extinguished 25° from vertical edge. Some crystals exhibit absorption with single nicol. |
| $Ce_2(SO_4)_3+9H_2O$ .. | 15 | ,, ,, | H | (*a*) Prisms with pyrl. terminations.<br>(*b*) Radiating fibres like spherulites.<br>(*c*) Radiating tables with the habit of a zeolite. | 1st order. | (*a*) and (*b*) at *R.L.* to *e*.<br>(*c*) ‖ to *e*. | |
| **Cobalt.** | | | | | | | |
| $CoSO_4+4H_2O$ . .. | 16 | | — | A peach-blossom coloured powder. | | | |
| $CoSO_4+6H_2O$ . .. | 17 | | M | In crystals. | | | |
| $CoSO_4+7H_2O$ . .. | 18 | Bieberite or cobalt vitriol. | M | Crystalline crusts made up of obscurely-shaped granular crystals, with occasional 4- or 6-sided tabular crystals. | 2nd order. | About 30° from *e*. | Dichroic. Rose-pink to amber. Relief sharp. |
| $CoSO_4K_2SO_4+2H_2O$ | 19 | — | Tr | | | | |
| $CoSO_4.K_2SO_4+$ $+6H_2O$ | 20 | — | M | Large tabular crystals with six, eight, or more faces, two or more corners often truncated; edges sometimes bevelled. | So high that a double *Q.W.* is sometimes required. | (*a*) Within a few degrees of *R.L.* to *e* in approximately rectangular prisms.<br>(*b*) Within a few degrees of a line bisecting the acute angles in prisms of sphenic habit. | Extinction in (*a*) within a few degrees of *e*, in (*b*) within a few degrees of line bisecting acute angles. Dichroic in rose-pink and amber colours. Zonal structure. Twinning not uncommon. |

*Remarks.*

*No.* 11.—The crystals (*a*) have one of the acute angles pointing outwards: the other is at the centre of radiating group. The rib approximately bisects the acute angles. Many of the crystals strongly recall fig. 528 Dana's system, 5th Edn. The rib is apparently the junction of $-1 : -1$ and I : I.

*No.* 12.—Is obtained by dissolving the dioxide in dilute $H_2SO_4$ and evaporating in a vacuum over $H_2SO_4$. Ceric sulphate is decomposed by water with formation of basic salts, which vary in composition according to the quantity of water present. It forms double salts with sulphates of the alkali metals, such as $Ce(SO_4)_2+2K_2SO_4+2H_2O$, small yellow monoclinic crystals.

*No.* 13.—Separates from a warm solution. It dissolves in six parts of cold and sixty parts of hot water. Also in hot $H_2SO_4$, which on cooling throws down small crystals and long needle-shaped prisms, which are re-dissolved after standing for some hours.

*No.* 14.—Separates from a concentrated solution. It occasionally exhibits multiple twinning.

*No.* 15.—Separates principally from dilute solution, but generally both 14 and 15 will be found on the same slide. Solution 1 in 6. Cerous sulphate forms several potassium cerous double salts, as—

$$3K_2SO_4+Ce_2(SO_4)_3Ce_2(SO_4)_3+2K_2SO_4+3H_2O \text{ and } Ce_2(SO_4)_3+K_2SO_4.$$

Sodium and ammonium sulphates also form double salts with cerous sulphate.

*No.* 16.—Deposited when a concentrated solution of cobalt sulphate is passed into $H_2SO_4$.

*No.* 18.—Soluble in twenty-four parts of cold water. Rose colour deepens on heating; crystal becomes opaque.

*No.* 20.—On heating, the rose-coloured crystals become reddish violet. Some of the rose-red crystals show a positive bisectrix.

(To be continued).

# ORIGIN OF OXYGEN IN THE EARTH'S ATMOSPHERE.

By Dr. T. L. PHIPSON, F.C.S., &c.,
Graduate of the Faculties of Science and Medicine of the University of Brussels.

In 1791, when Priestley's house was burut by the Birmingham mob, and he saved his life by escaping in my grandfather's* carriage, a considerable amount of valuable silver plate, &c., was carried off at the same time, but none of the still more valuable MSS., the results of years of labour. These were destroyed, together with the entire library and laboratory. It is therefore impossible to say how far he may have pushed his investigations with regard to the mutual dependency of plants and animals, after discovering, some twenty years previously, that a sprig of mint vegetating for a few days in air vitiated by a burning candle, restored the purity of that air sufficiently to allow the candle to burn in it again.

In the seventh edition of the "Introduction to Botany." by Sir J. E. Smith. F.R.S., edited by William Hooker (1833, p. 104), the author, alluding to the absorption of carbonic acid by plants and its replacement by oxygen, says:—"This beautiful discovery, for the main principles of which we are indebted to the celebrated Dr. Priestley, shows a mutual dependence of the animal and vegetable kingdoms on each other which had never been suspected before his time."

It is not probable, however, that Priestley could have made much further advance owing to the backward state of chemistry in his day, and to his zeal for religious and political discussions. It was reserved for the persevering researches of the Swiss chemist, Theodore de Saussure, and to the splendid genius of Justus von Liebig, to demonstrate this mutual dependency in all its striking realities. Yet it is greater than even Liebig imagined.

In discussing recently the views of the late Prof. C. J. Koene, of Brussels University, on the Chemical Constitution of the Earth's Atmosphere from remote geological periods to the present time, I have mentioned the results of certain experiments which I had made with the view of elucidating this interesting question.

I found that minute microscopic plants (*Protococcus pluvialis* and *P. palustris*) could be easily transformed, so to speak, into manufacturers of oxygen gas. I grew several kinds of plants in pure carbonic acid, and found that it did not kill them at once, as it would kill an animal, but that they lived in it for some time, though they did not prosper. In an atmosphere of hydrogen gas they lived and prospered, but the hydrogen was slowly absorbed until it had all disappeared, or nearly so, and the plants got covered with water.

In the next place I exposed my plants to an atmosphere of pure nitrogen, and to Koene's primitive atmosphere (nitrogen and carbonic acid), and I found that, in both cases, vegetation was remarkably healthy and even luxuriant for a lengthened period. A small plant of *Convolvulus arvensis* (having its roots in the soil, or in water containing ample carbonic acid and mineral ingredients) vegetated in an atmosphere of pure nitrogen for ten days —from June 22nd to July 2nd. I then let in carbonic acid (an equal volume), which in twenty-four hours was absorbed by the water to the extent of about one-half, so that the artificial atmosphere on the second day consisted of about 3 vols. of nitrogen and 1 vol. of carbonic acid. In this the vegetation became truly luxuriant from July 2nd to 15th, and would doubtless have continued very much longer had not the experiment been stopped to analyse the gas, and because the plant had reached the summit of the receptacle and was pressing against the glass.

To give the results of these observations in as few words as possible, I may state that the plant absorbs carbonic acid by the roots, whilst it secretes oxygen by the leaves, so that after awhile the nitrogen atmosphere contains a certain quantity of oxygen, and in time it would, no doubt, approach to the composition of ordinary atmospheric air.

Now, if I endeavour to go back to the primitive ages of the globe, I find that there was probably a period at which the heat was so intense that no compounds could exist; the matter of the earth then existed in the state of free elements, or, according to my own theory,* in the state of atoms, all identical. As the temperature decreased, compounds of all kinds were formed according to the laws of affinity, and finally there remained surrounding the solidified surface of the earth an atmosphere of nitrogen, a substance which is known to have little or no tendency to combine directly with other substances. That there was no free oxygen in this ancient atmosphere is evident from the presence of various oxidisable substances in the primitive rocks, as I have before remarked. It is *into this primitive atmosphere of nitrogen that plants have poured oxygen, year after year, for countless myriads of ages, until it has attained the composition which it has at the present day.*

There may have existed, as Koene admitted, more or less carbonic acid at certain remote periods in the history of the earth's atmosphere; but it is unlikely ever to have predominated, from the fact that it would have been absorbed by the waters, and from my experiments, which show that some of our modern plants having their roots in the soil, or in water containing carbonic acid and the necessary mineral elements, will live in an atmosphere of nitrogen.

I am therefore led to the conclusion that *the original atmosphere of our globe consisted of nitrogen alone*; and that *the oxygen of the atmosphere is the product of vegetable life* (which must necessarily have preceded animal life). The production of oxygen by *Protococcus pluvialis*, alluded to above, is a symbol of what took place in the primitive ages of the Earth. It will be seen by my former papers that carbonic acid must be looked upon as a volcanic product extensively diffused through the earth's strata. The primitive atmosphere of nitrogen would doubtless derive abundance of carbonic acid from volcanic action, which continued to be intense until after the coal period, and appears to have gradually diminished from that period to the present time, though it is still very active.

Putney, July 22, 1893.

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* Thomas Phipson, of Birmingham, into whose family Dr. Priestley married, and who helped him in his political work.

* Phipson, "Outlines of a New Atomic Theory," 4th ed., 1884.

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# ON POISONING BY BADLY-TINNED AND UNWHOLESOME FISH.

By Dr. A. B. GRIFFITHS, F.R.S. Edin., &c.

The poisonous ptomaines, formed from albumenoids during the decomposition of food, produce symptoms of poisoning, &c., which are said to be referable to the digestive and nervous systems. These symptoms manifest themselves at periods varying from a few hours to several days after eating the food. The symptoms produced by this class of ptomaines are the following, among others: —Unpleasant taste in the mouth, headache, vomiting, diarrhœa, salivation, dyspnœa, paralysis, and death. Several ptomaines render the heart's beats slow and weak, and in some cases of poisoning by unwholesome fish the symptome resemble those of poisoning by atropine.

Poisoning by unwholesome foods too frequently escapes notice; nevertheless every analyst or medical man who is careful of his scientific dignity should possess a thorough knowledge of the properties of the ptomaines, which have now quite a literature of their own.

Numerous deaths have occurred in England (see Griffiths in Chemical News, vol. lxii., p. 17; and the reports in *Daily Graphic*, Nov. 25th, 1892; *Daily News*, Nov. 22nd, 1892, and April 22nd, 1893), on the Continent, and in America, from eating unwholesome foods; and it has been shown that the poisonous properties of such foods are due to the action of microbes on the proteids contained in the foods. It may be stated that these poisonous properties are due to certain ptomaines or animal alkaloids. The ptomaines are produced during the putrefaction or decomposition of animal substances. By the direct action of microbes, the proteids are disintegrated, with the formation of ptomaines among other products. It will be seen, from this remark, that the ptomaines are not secreted or excreted by microbes, for they are the *residua* after microbian action. To explain the action of microbes on organic matter generally: let $a_3b_4c_5d_3$ represent the composition of the medium in which certain microbes live, and let $a_2b_2c_3d_1$ represent the food extracted from such a medium by the microbes for their nourishment; it therefore follows that $a_1b_2c_2d_2$ will represent the residue or the products of the microbian action—be it fermentation, nitrification, the production of ptomaines, &c.

It should also be borne in mind that the idea of ptomaines *without* microbes is inconsistent with an impartial study of facts. It is true that a suitable filtration (*e. g.*, through porous porcelain) will separate a ptomaine from its microbe; but when this microbe is separated from the original liquid, and transferred successively to nourishing media, so as to purify it from every foreign element, it continues to produce its characteristic ptomaine (or ptomaines), which is produced at the expense of the culture fluid. There is no true ptomaine without microbes, any more than there is ergotine without *Claviceps purpurea*, vinegar without *Bacterium aceti*, or alcohol without certain species of the *Saccharomycetes*.

Such is our preliminary remarks concerning the ptomaines; we now proceed to describe a new ptomaine which we have extracted, from *putrid sardines*, by the following process:—

The putrid mass was boiled with water, filtered, and the filtrate precipitated with subacetate of lead. This precipitate was filtered off, a current of $H_2S$ passed through the filtrate, and the plumbic sulphide separated by filtration. The filtrate was concentrated by evaporation, and then extracted with amylic alcohol. The amylic solution was repeatedly treated with water, then concentrated, acidulated with $H_2SO_4$, and repeatedly shaken with ether, which removes the oxy-aromatic acids. Freed from ether, it was evaporated to a quarter of its volume, and thus volatile fatty acids were driven off. The $H_2SO_4$ was precipitated by baryta, and the precipitate removed by filtration. The excess of baryta was precipitated by a current of $CO_2$, and this was also removed by filtration. The fluid was heated for some time on a water-bath, cooled, and precipitated with $HgCl_2$. The precipitate was washed and decomposed by $H_2S$; the mercuric sulphide was filtered off, and the filtrate concentrated. The hydrochloride of the ptomaine was subsequently deposited in the crystalline condition. It was dissolved in water, and then treated with pure calcium hydroxide, which liberated the base. The ptomaine was separated by chloroform, in which it is soluble; and it was finally purified by washing with alcohol and water.

This new ptomaine is a white crystalline substance, soluble in water, and has a slight alkaline reaction. It is precipitated by hydrochloric acid in the form of a white crystalline hydrochloride. Platinic and auric chlorides precipitate this ptomaine, and the resulting platino-chloride and aurochloride are yellow crystalline compounds. This base produces with phosphomolybdic acid a greenish precipitate, with phosphotungstic acid a yellowish-white precipitate, and with picric acid a yellow one. It is also precipitated by silver nitrate and Nessler's reagent. Analyses of this base gave the following results:—

0·378 grm. of substance gave 0·9669 grm. of $CO_2$ and 0·2034 grm. of $H_2O$.

0·2213 grm. of substance gave 14·1 c.c. of N.

| | Found. | | Calculated for $C_{11}H_{11}NO_2$. |
|---|---|---|---|
| | I. | II. | |
| Carbon .. .. | 69·77 | — | 69·84 |
| Hydrogen .. | 5·98 | — | 5·82 |
| Nitrogen .. .. | — | 7·45 | 7·40 |
| Oxygen .. .. | — | — | 16·94 |

The above figures correspond with the formula—

$$C_{11}H_{11}NO_2$$

for this new ptomaine.

This base which has been named *sardinine*, is poisonous —producing vomiting, diarrhœa, and death; and there is little doubt that it is the cause of the poisoning which results from eating putrid sardines or sardines which have been badly tinned.

It may be useful to give a list of the ptomaines which have been extracted from the products of bacterial putrefaction of certain fishes, &c.:—

(1.) Parvoline, $C_9H_{13}N$, from mackerel (Gautier and Etard).
(2.) Hydrocollidine, $C_8H_{13}N$, from mackerel (Gautier and Etard).
(3.) Scombrine, $C_{17}H_{38}N_4$, from mackerel (Gautier and Etard).
(4.) Muscarine, $C_5H_{13}NO_2$ (Brieger).
[*](5.) Gadinine, $C_7H_{16}NO_2$, from cod (Brieger).
(6.) Ethylenediamine, $C_2H_8O_2$, from cod (Brieger).
(7.) Mytilotoxine, $C_7H_{15}NO_2$, from mussels (Brieger).
(8.) Sardinine, $C_{11}H_{11}NO_2$, from sardines (Griffiths).
(9.) Collidine, $C_8H_{11}N$, from cuttle-fish (De Coninck).
(10.) Coridine, $C_{10}H_{15}N$, from cuttle-fish (De Coninck).

In addition to "fish-poisons," it may be mentioned, *en passant*, that Lewis (Chemical News, vol. lxvii., p. 52) believes that the twenty cases of poisoning in America, which resulted from eating tinned beef (in 1892), were due to neuridine ($C_5H_{14}N_2$); and the poisoning which sometimes results from eating unwholesome cheese, ice-cream, &c., has been proved to be due to a ptomaine which is named tyrotoxicon ($C_6H_5N_2$) by Vaughan.[†]

In conclusion, there is no doubt that the ptomaines play an important part in most cases of poisoning from eating unwholesome food, and it is of primary importance that analysts, medical men, and others, should make themselves thoroughly familiar with the properties of these curious products of putrefaction.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.[‡]

By VICTOR SCHUMANN, of Leipzic.

The extension of the ultra-violet spectral region is in close connection with the invention of photography and the discovery of fluorescence. The main region of the ultra-violet light was opened up with the aid of fluorescence, but in its exploration photography has given brilliant evidence of its superiority. The fluorescence method of observation has since gradually lost ground, whilst the efficacy of sensitive plates in the ultra-violet region has increased.

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[*] Gadinine is non-poisonous.

[†] For further details concerning the ptomaines, see Griffiths's "Researches on Micro-Organisms" (Baillière), and "Manual of Bacteriology" (Heinemann); and the case of poisoning from eating ice-cream, reported in *Birmingham Daily Post*, Sept. 22, 1892.

[‡] From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur, Class.*, vol. cii., Part II., April, 1893).

The first observations in the ultra-violet region were undertaken by Edmond Becquerel (*Bibliothèque Universelle de Genève*, new series, vol. xxxix., pp. 341 to 367 [1842]), when he was studying the chemical action of the solar rays upon Daguerre plates. The solar spectra of Becquerel were formed, however, under the influence of the absorption of the glass, and they extended, therefore, only to Frauenhofer's P line.

Stokes, who recognised the greater transmissive power of quartz for light (*Phil. Trans.*, vol. cxlii., pp. 463 and 559 [1852]; vol. clii., pp. 599 to 619 [1862]), succeeded with prisms and lenses of quartz in following the ultra-violet of the solar spectrum to an extent which, measured from Frauenhofer's H line, was twice as long as the total visible spectrum. Still more surprising was his result with the electric light. The ultra-violet of his spark spectra extended to from six to eight times the length of the visible spectrum. The most refrangible rays of all substances were given by aluminium, the spectrum of which bounded the region of the smallest perceptible wave-lengths with a strongly luminous pair of lines of the wave-lengths 186·0 $\mu\mu$ and 185·2 $\mu\mu$. More strongly deflected rays do not seem to have been ever recognised in this region by Stokes and his successors. On the same day (June 19th, 1862), when Stokes submitted to the Royal Society of London his treatise on the above subject, W. A. Miller gave in to the same Society his no less important memoir "On the Photographic Transparency of Various Bodies, &c." (*Phil. Trans.*, vol. clii., pp. 861—887 [1862]).

Both these memoirs pursued the same object—ascertaining of the ultra-violet spectra of electric origin, and the behaviour of these spectra with substances in all three states of aggregation. But whilst Stokes made his observations with the aid of fluorescence, Miller utilised the photo-chemical action of the rays and took photographs of his spectra. The method of fluorescence showed itself strikingly preferable to the photographic method in one point: Stokes arrived at the wave-length 185·2 $\mu\mu$, whilst Miller did not get beyond the wave-length 202·4 $\mu\mu$. Miller afterwards, induced by Stokes, repeatedly attempted to photograph the remaining rays, but always without the desired result (*Phil. Trans.*, vol. clii., p. 882: 52 aluminium). The fluorescence spectrum retained here and in the sequel an advance which extended to the considerable extent of 172·0 $\mu\mu$.

This photographic ill success in the extreme ultra-violet excites hesitation if we see that L. Soret, Edouard Sarasin, and others, in their extensive researches, observed this part of the spectrum only by means of fluorescence. Hence it might seem as if photography was not suitable for the observation of the most refrangible light. Such an assumption is, however, completely refuted by the fact that Cornu made use of photography for determining the wave-lengths of the most refrangible rays of Mg, Cd, Zn, and Al (*Archives des Sci. Phys. et Nat.*, III. period, vol. ii., pp. 119—126 [1879]).

Cornu, driven to photography by the feeble light of his grating, adopted here the moist process, but, in contradistinction to Miller, he used the precaution of bathing the sensitised collodion plate in distilled water before its exposure to light. In this manner he obviated the most important photographic hindrance which the most refrangible rays encounter on a plate which has not been bathed, and secured at once a better photographic result.

A further difference between the experimental arrangements of Miller and Cornu deserves notice. The apparatus of these two investigators differed widely in their focal lengths. The focal distance of Miller's apparatus was by far the longer of the two. Hence the absorption of the rays in the air must have come into play to a different degree whilst the proof was taken. The experimental arrangement of Cornu was consequently preferable also in this respect.

The photographic result of Cornu for the smallest wave-lengths seemed to open out a favourable prospect for the investigation of the ultra-violet region which had hitherto been neglected. Unfortunately the future did not answer this expectation. Experimental hindrances of an unknown kind have again estranged the region of the most refrangible rays of aluminium (198·8—185·2 $\mu\mu$) from photographic spectroscopy. The majority of all researches extends even at present to the neighbourhood of the most refrangible lines of cadmium (226·55—214·41 $\mu\mu$), and only occasionally the region of the most refrangible lines of zinc (214·41—198·8 $\mu\mu$) is taken into consideration. This phenomena is the more striking as since Cornu's investigations spectroscopy has obtained, in silver bromide gelatin dry plate, an auxiliary which throws into the shade, in every respect, all the results of the collodion plates formerly employed.

The gelatin plate has for a series of years conferred invaluable services upon spectral research. It is only since its introduction that photographic observation has made successful way in spectroscopy; with it the conviction has been secured that a study of the visible spectrum alone does not suffice for the comprehension of spectral processes, but that there is required as thorough a knowledge of the invisible spectral regions, especially the ultra-violet. In recent observations this necessity is taken into account wherever possible.

In view of the fruitfulness of the efforts in the ultra-violet regions which recent years have matured, it seemed to me desirable and highly remunerative to open up to photographic study the remaining ultra-violet, as far as the wave-length 185·2 $\mu\mu$, by means of a more suitable process than those hitherto applied, and at the same time to consider the extension of this region of observation in the direction of greater deviation.

For several years I have been approaching the execution of this thought. My task resolved itself into two portions. The first was the photography of the spectral region between the wave-lengths 231·35 and 185·2 $\mu\mu$; the second was the opening up of the unknown region beyond 185·2 $\mu\mu$.

The present report discusses the first part of this work, and at the same time the preliminaries for the second.

Its results, as also the representations of the apparatus used and of the spectra obtained, will form the contents of a brief subsequent second report.

Each of these portions has engaged a considerable time, and the second portion still awaits completion.

If I now venture upon publicity with the results already obtained, although years must probably elapse before the completion of my work, the step has been induced, on the one hand, by the requests of a number of eminent physicists to whom I have had the honour of submitting my chief results, and, on the other, by my own wish to bring the facts ascertained to the knowledge of the most extended circles.

(To be continued.)

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending June 30th, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, July 6th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The quality of the water supply during June has been very good, and bears a close relationship to that of the supply during May. Towards the end of the month the long drought began to break, but the rainfall was too insignificant in quantity to make itself apparent in the composition of the waters. During June the average rainfall for Oxford, taking a mean of twenty-five years, is 2·21 inches, whereas the rainfall during the past month has only been 0·77 inch, showing a deficiency of 1·44 inch. Most of this fall took place during the latter part of the month.

In our report for May we drew attention to the steady and appreciable decrease in the proportions of common salt, oxidised nitrogen, and hardness of the Thames-derived waters. The following Table shows that the supposed deterioration in quality of the river water consequent on greatly deficient rainfall and high temperature has no foundation in fact, the increased activity of fluviatile vegetation more than counteracting any slight excess of mineral matter which might theoretically be present.

| 1893. | Common salt per gallon. | Nitric acid per gallon. | Degrees of hardness per gallon. |
|---|---|---|---|
| March.. .. .. .. | 2·167 | 0·931 | 16·80 |
| April .. .. .. .. | 2·181 | 0·888 | 15·11 |
| May .. .. .. .. | 2·196 | 0·611 | 14·66 |
| June .. .. .. .. | 2·132 | 0·601 | 14·74 |

The organic carbon and the oxygen required for oxidation were practically the same as in the two previous months, the difference showing an excess only in the third place of decimals.

The turbidity, or dull appearance, which has been recorded in five of the samples supplied by the Grand Junction Water Company was due to suspended clay particles, and is accounted for by temporary local disturbances in the mains resulting from the fixing of fire hydrants in accordance with the requirements of the London County Council. The turbidity was only local, samples from the works on these days being perfectly clear. With these exceptions, all the samples were well filtered, clear, and bright.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

**Le Chatelier's Thermo-element for the Measurement of High Temperatures.**—Emilio Damour.—An exposure of five seconds is sufficient for measuring the temperature of a space. H. M. Howe (*Mining Journal*) recommends Le Chatelier's instrument for industrial uses. L. Holborn and W. Wien have compared (*Annalen der Physik und Chemie*) the thermo-element with the air thermometer. The mean difference between separate experiments is 5°. A thermometer on the principle of the differential air thermometer has been described by H. L. Callendar, German patent No. 62,796.—*Zeitschrift fur Analytische Chemie*, xxxii., Part 3.

## NOTICES OF BOOKS.

*The Newer Chemistry.* ("Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik"). Von Dr. Walther Nernst, A. O. Professor au der Universität, Göttingen. Mit 26 Holzschmitten. Stuttgart: Verlag von Ferdinand Enke, 1893.

To a large number of chemists this excellent book will be open only in part. Unfortunately, too, this list will include many of the younger generation of chemists, for whom the book has a special significance. The title gives the reason. Of course, so far as the ordinary subject-matter of theoretical chemistry is dealt with, and expressed in everyday language, the book will find many readers, but such reading is not competent to bring out the real value of the work. It is not intended for elementary students. It has a particular purpose, and for the accomplishment of this purpose within allotted limits, much that is elementary must be assumed and passed over without special treatment, but nothing which could aid in bringing out the commanding position of thermodynamics and the kinetic theory of gases as foundation stones in the structure of chemistry has been omitted, and from this standpoint the book is consistent, complete, and fairly exhaustive.

As previously remarked, the real value of the work will not appear to the cursory, or even to the careful but non-mathematical, reader. In order to read it intelligently, an elementary knowledge of the higher mathematics will not suffice. It must not be inferred that the pages of Dr. Nernst's book bristle with integration signs; there is, on the contrary, a notable freedom from long and involved expressions, and there are abundant signs that it was the author's aim to avoid mathematical formulæ so far as possible; but, after all this is said, it is nevertheless true that unless the reader is familar with the fundamental mathematical formulæ and equations of thermodynamics and physics generally—unless he has, withal, considerable freedom in mathematical thinking, his reading will be rather slow and painful. The style is quite concise, and the extent to which the higher analysis has been utilised has enabled a vast amount of material to be put within a comparatively small space. In this connection, some remarks of Ostwald, in the preface to his "Outlines of General Chemistry," as translated by Walker, may be quoted:—

"The task has been all the more difficult that the course of study still pursued by the average chemist has laid upon me the necessity of avoiding the employment of higher mathematics. When possible, I have applied graphic methods. When a clear proof could not be given in an elementary way, I have contented myself with simply stating the result. Of course one can, with the aid of more or less cumbrous mathematical apparatus, give an 'elementary' proof of almost anything, but experience has shown that such diffuse page-long calculations are of no real aid to the comprehension of the subject. Another reason that has led me to adopt the above mode of treatment is that the reader who has only an acquaintance with elementary mathematics may be brought to see the necessity of acquiring at least the rudiments of the higher analysis. Without such knowledge it is possible (as I have endeavoured to show in the following pages) to understand both the methods and the results of general chemistry; but for successful work in this field such knowledge is indispensable."

It would be well for every student to lay these words well to heart. The expenditure of time needed to gain the necessary mathematical training is not great, and there is no good reason why so fruitful and important a line of study should be so often omitted. The case is somewhat different with those who have to "brush up" mathematics grown rusty by disuse. In the face of all that has been said the question *cui bono* will certainly be raised, and the claims of the methods and results of the so-called "Physical Chemistry" to particular attention will be, as they have been, more or less called in question. Whatever may be thought on this point, we certainly have to thank the modern chemistry for a host of ideas, which in their development have been wonderfully prolific; and the methods of thought it has brought in will, without doubt, exercise upon chemistry much such an effect, both in kind and degree, as did the introduction of the Cartesian philosophy upon the ancient geometry.

There is, for the present at least, little danger of chemistry becoming too speculative. The smoke of the battle between the unitary and dualistic systems has hardly cleared away, and we still have with us many of those who saw, and had active part in, that battle. It has left upon their minds an impression which will not soon be blotted out, but of which the younger generation have only a faint conception. They will not be likely to speculate too freely, or lose sight of the essentially inductive nature of the science; but the probability is that history will repeat itself. Man does not learn wisdom from the past. He prefers the hard teaching of experience, and the younger chemists will probably have to learn their own lesson from their own experience. Moreover, it is true that while the characteristic theories of "Physical Chemistry" are perfectly safe under their present expounders, the case may be quite different when they are more general subjects of investigation. The theories of one generation do not always prosper in the hands of the next. From this point of view it is very desirable that attention should often be called to the aspect of the new methods and results as they appear *in situ* in the structure of our chemical philosophy, and the work now under consideration does so in a very satisfactory manner.

The most conservative will find in it nothing which by its infusion into chemical philosophy will detract in the least from its completeness and consistency.

In conclusion, it is good news that Dr. Nernst's book is to be translated, for the German is a trifle peculiar, and it is certainly a fact that most students, in America at least, read German with very much less fluency than English, and the majority of German works of the calibre of the present one remain unread until they are translated.—Joseph Torrey, Cambridge, Mass., U.S.A.

*Lecture Notes on Theoretical Chemistry.* By Ferdinand G. Wiechmann, Ph.D. New York: John Wiley and Sons, 1893. Pp. xiv.—225. 12mo. Ill.

The author of this well-written volume, who holds the position of Instructor in Chemical Physics and Chemical Philosophy at the School of Mines, Columbia College, New York City, is already favourably known by his work on Sugar Analysis. In the present volume the author offers a general view over the wide domain of chemical theory, exhibiting very clearly the correlation of the many lines of research along which investigations of the questions of theoretical chemistry are conducted, as well as pointing out the practical bearings of its teachings on problems constantly occurring in the application of chemical knowledge.

The treatise does not, however, offer an exhaustive discussion of the subject. The scope is well shown by the headings of the chapters:—I. Introduction; II. Specific Gravity; III. Nomenclature and Notation; IV. Atoms, Atomic Mass, Valence; V. Chemical Formulæ; VI. Structure of Molecules; VII. Chemical Equations and Calculations; VIII. Volume and Weight Relations of Gases; IX. The Periodic Law; X. Solutions; XI. Energy, Chemical Affinity; XII. Thermal Relations, Thermo-chemistry; XIII. Photo-chemistry; XIV. Electro-chemistry.

In Chapter III. Dr. Wiechmann pourtrays briefly the development of the language of chemistry, with appropriate illustrations of the systems in use at different periods. He adopts the "Rules for Spelling and Pronouncing Chemical Terms" recommended by the committee of the American Association for the Advancement of Science. In Chapter VI. stereochemistry receives brief notice. In Chapter VII. three methods of writing chemical equations are clearly set forth. Stoichiometry is made prominent throughout, but the book is not loaded up with problems "in view of the fact that several excellent collections have been recently published." In Chapter XIV. Arrhenius's theory of electrolytic dissociation is described: In Chapter IX. Newlands receives credit for his Table.

Throughout the work the author pays due regard to the historical method of unfolding theories. He acknowledges his indebtedness to the works of Kopp, Ostwald, and Muir, and he appends an excellent bibliography of 193 titles. The book concludes with a very full index of subjects, as well as an index of names cited.

This little volume will be welcomed by all teachers who appreciate clearness and accuracy of statement, as well as modern methods of presentation. The book is fully abreast of the times.—H. C. B.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

### *Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxii., Nos. 1 and 2.

**Determination of Sulphur in Fuel by the Eschka Process.**—Dr. Hundeshagen has reopened this subject in the *Chemiker Zeitung.* He concludes that with rare exceptions the Eschka process yields exact results with ordinary coals, but with coals rich in volatile sulphur compounds (and probably in nitrogen) the result may be too low. Certain lignites, if treated according to the Eschka process, yield an emission of ammonium sulphide sufficient to blacken instantly a lead-paper.

No. 3, June, 1893.

**Sterilisation of Drinking Water by the William Kuhn System.**—The author contends that water for a public supply should be absolutely sterilised. This can be effected by heat alone, the water being kept for twenty minutes at a temperature of 110°. The cost of the operation on the large scale does not exceed 0·035 franc per hectolitre. Such water, however, must not be allowed to remain in the reservoirs, &c., for longer than twenty-four hours.

### *Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 13.

**Determination of Phosphoric Acid.**—M. A. Villiers and Fr. Borg.—This memoir will be inserted in full.

**Observations on the Determination of Manganese by means of Potassium Permanganate, and on the Manganese Permanganate of Antony Guyard.**—Alex. Gorgeu.—This paper will also be inserted in full.

**On the Native Manganese Oxides, Polianites, and Pyrolusites.**—A. Gorgeu.—The author here undertakes to determine the exact composition of the native manganese peroxide known as polianite, and pyrolusite.

**Absorbent Action of Cotton upon Dilute Solutions of Mercuric Chloride.**—Léo Vignon.—In these solutions cotton seems to dissociate mercuric chloride according to the equation $HgCl_2+H_2O=HgO+2(HCl)$. The cotton combines with the mercuric oxide in virtue of its acid function, whilst it simply absorbs hydrochloric acid without entering into combination.

**Determination of Mercury in Dilute Solutions of Mercuric Chloride.**—Léo Vignon.—We take, *e.g.*, 50 c.c. solution of sublimate at 1 part in 1000; we add 5 c.c. of pure hydrochloric acid at 22°, and 10 c.c. of a saturated clear solution of hydrogen sulphide. We obtain a yellow precipitate, which quickly becomes black, and filter on a filter which has been previously weighed to one-tenth of a m.grm. The precipitate is washed, dried, and weighed. It is useful to operate in comparison with a check filter, through which we have filtered a mixture of 50 c.c. of distilled water, 5 c.c. of hydrochloric acid, and 10 c.c. of $H_2S$, which is washed like the foregoing. The weighing of this check-filter, of the same size and the same paper as the filter containing the mercury sulphide, furnishes a means for correction.

**Action of Cotton upon Sublimate Absorbed in Dilute Solutions.**—Léo Vignon.—The author concludes that bleached cotton, plunged into dilute solutions of sublimate, fixes mercuric oxide in excess over the hydrochloric acid. Cotton dried at the common temperature, then steeped in water, after some days gives up only a part of its mercury in the state of $HgCl_2$ and of hydrochloric acid. It retains mercuric oxide, HgO, and mercurous chloride, $Hg_2Cl_2$.

**Syntheses with Aluminium Chloride.**— P. Genviesse.—Already inserted.

**Cause of the Variation of the Rotatory Power in certain Solutions of Optically Active Substances with Time and Dilution, and on the Rotatory Power of Amorphous Substances.**—A. Béchamp. — This extensive memoir does not admit of useful abstraction.

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Erratum.—P. 35, col. 1, line 5, *for* "D.Ph., Cantab.," *read* "D.P.H., Cantab."

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1758.

## THE DETERMINATION OF MANGANESE BY OXYDIMETRIC METHODS.

By ADOLPHE CARNOT.

When the state of oxidation of manganese is exactly known we may find the proportion of the metal by determining the oxygen. The determination of the available oxygen may be effected quickly and satisfactorily either by a gasometric method founded on the mutual decomposition of manganese peroxide and of hydrogen peroxide, the liberation of oxygen double the quantity of that which is to be ascertained, or by one of the numerous oxydimetric methods which have been proposed. The best of these, in despatch and accuracy, seems to me that which employs standard solutions of oxalic acid and of permanganate.

But to be warranted in substituting the determination of available oxygen for that of manganese, we must be sure of the relative proportion of the two elements.

I. Ignition in contact with air, sufficiently prolonged and at a very high temperature, converts the different oxides into a compound which has almost exactly the formula $Mn_3O_4$. But different circumstances, especially the contact of reducing agents or the presence of powerful bases, such as the alkalis or the alkaline earths, may modify the composition. It must also be remarked that the determination of 3 equivalents of manganese has to be deduced from that of a single equivalent of oxygen, which interferes with the precision of the process.

II. The solution of manganese in nitric acid, followed by evaporation to dryness and the careful ignition of the residue until all the nitrous vapour disappears, yields a black oxide which is commonly considered as binoxide, but which has really a composition remote from $MnO_2$. We may approach accuracy by repeating the evaporation with nitric acid two or three times, and igniting below 200°; but notwithstanding these precautions the degree of oxidation remains uncertain.

III. If we dissolve manganese in nitric acid, and introduce by small portions crushed potassium chlorate into the hot solution, we obtain a black residue which has the composition $MnO_2$. Other metals are generally dissolved, though the iron is not immediately eliminated.

The residue, which is insoluble in nitric acid alone, is easily dissolved with that acid along with hydrogen peroxide. By evaporation and repeated addition of concentrated nitric acid and potassium chlorate, we may arrive at a product not containing more than a minimum of iron, and in which the manganese is entirely present as $MnO_2$.

I have satisfied myself that after a good washing with water, cold at first and then boiling, the binoxide obtained, either by one precipitation or by two precipitations, may be accurately determined by the oxydimetric method.

IV. The results are still more certain by the method with hydrogen peroxide and ammonia, a method which I have summarily explained in 1888, and on which I have made since that date numerous series of experiments.

On pouring into the solution of manganese hydrogen peroxide, either in excess or only in a sufficient quantity, and then quickly supersaturating with ammonia and heating for some minutes to ebullition, we obtain a deep brown precipitate, in which the degree of oxidation of the manganese is very exactly expressed by the formula $Mn_6O_{11}$ or $5MnO_2,MnO$.

The volumetric and gasometric determinations have shown that 6 equivalents of manganese correspond very accurately to 5 equivalents of available oxygen.

The operation being extremely simple and rapid, the method has seemed to me to admit of frequent applications, and I have carefully studied the influence of the various circumstances which may occur.

I found that ammoniacal salts (nitrate, hydrochlorate, and especially acetate), in considerable quantities (from 10 to 20 grms.), interfere with the formation of the peroxide $Mn_6O_{11}$, but their influence may be counteracted by the use of a larger quantity of hydrogen peroxide.

If the precipitation of manganese is effected in presence of salts of copper, zinc, nickel, or cobalt, a small portion of these oxides, although soluble in ammonia and the ammoniacal salts, is retained by the manganese binoxide, with which they tend to form manganites comparable to the manganese manganite, $5MnO_2,MnO$. But we can cause them entirely to disappear, and obtain the pure manganese peroxide, $Mn_6O_{11}$, by re-dissolving the precipitate upon the filter in very dilute nitric acid and hydrogen peroxide, and precipitating again with ammonia. With large quantities of copper, nickel, or zinc, three precipitations are sufficient, but with cobalt five precipitations are required. We may then execute very accurately either the volumetric or the gravimetric determination of manganese.

Iron oxide, which accompanies manganese in its precipitation and interferes with its gravimetric determination, does not affect the accuracy of its volumetric determination unless it predominates. If there is more iron than manganese the determination is less satisfactory. It is, then, necessary to eliminate the main part of the iron by treatment with nitric acid and potassium chlorate (III). The insoluble residue, dissolved in nitric acid and hydrogen peroxide, and re-precipitated with ammonia, is then perfectly suitable for volumetric or gasometric determination.

This process succeeds well with ores of manganese and iron, cast metal, spiegel, and ferro-manganese.

V. We may also precipitate manganese as peroxide by the use of bromine and ammonia in the cold, taking care to leave the bromine to digest for a long time with the liquid almost neutral, or, for greater despatch, repeating the addition of bromine and ammonia twice. The manganese is deposited as an oxide, nearly black; but before proceeding to the oxydimetric determination it is necessary to submit the precipitate to a very prolonged washing with boiling water. This method is less to be recommended than the foregoing, which is more expeditious and more trustworthy.—*Comptes Rendus*, cxvi., p. 1375.

## THE SEPARATION OF COPPER FROM BISMUTH.

By ALEX. CLASSEN.

Ed. Smith and J. Salter report (*Zeits. fur Anorganische Chem.*, No. 6) concerning experiments which they have made for separating copper and bismuth in solutions containing nitric acid, and refer to statements in my text-book on Electrolysis. I wish here to make known that the method itself, as also the quotations on the strength of current, the nitric acid, &c., for its execution are not due to me. The communications on the separation of these metals, at the passages indicated by Smith and Salter, have been transferred from the second edition of the book to the third edition without further remarks, though in two other passages of the book (pp. 80 and 186) it is expressly pointed out that in presence of bismuth portions pass into the copper precipitate. On p. 186 it is simultaneously mentioned how bismuth is to be separated from copper.

It has long been known that, in presence of bismuth, copper is not deposited pure, as has been confirmed by the researches of W. Hampe and V. Klobulow. Three years ago I utilised the fact that bismuth can be deposited electrolytically from a solution containing free nitric acid for obtaining pure bismuth; and I pointed out that, along with metallic bismuth on the negative electrode, a coating of bismuth peroxide is obtained on the positive electrode, which, however, disappears towards the end of the decomposition, as Smith and Salter have recently confirmed. These chemists have further occupied themselves with experiments for separating bismuth from lead in a solution containing nitric acid, and they have found that the lead peroxide obtained is always bismuthiferous. I had previously made the same observation in connection with obtaining bismuth in a state of purity. In the work referred to it is stated:—"If the bismuth contains lead it is by degrees totally deposited as peroxide on the positive electrode along with bismuth peroxide. No separation of metallic lead takes place at the negative electrode provided there is a sufficiency of nitric acid and that feeble currents are employed.

As Smith and Salter project further experiments on the behaviour of different metals with the current in presence of nitric acid, and have already announced a separation of mercury from bismuth, I remark that as far back as 1880 I have shown (*Berichte*, xix., 323) that these metals cannot be separated in the manner mentioned. These facts are here especially pointed out with reference to the circumstance that the proposals for the separation of bismuth from lead and mercury have been already transferred to my book without criticism.—*Zeitschrift fur Anorganische Chemie*, iv., p. 234.

## SOME NEW LABORATORY FITTINGS.*

By G. A. GOYDER, F.C.S., Analyst and Assayer.

A modified form of sulphuretted hydrogen apparatus has been fitted up both in the assay and students' laboratory, and as they have been found to work very economically, and with less trouble than those previously in use, and with a minimum of smell, a description of them is appended.

### *Construction.*

The construction of the apparatus may be readily seen from Fig. 1.

The stopper in A should fit loosely.

The tap A may be replaced by a pinchcock.

The valve B may be made by bending a 10 c.c. or 15 c.c. pipette, and it is joined to A by a piece of rather stout indiarubber tubing, the ends being tightly tied over the glass. This remark applies to all the indiarubber tube connections used. The lower end of B is drawn out, as at C, so that only a very thin stream of acid can run through it: B is fixed in the neck of B by means of a short indiarubber stopper.

B is most conveniently made from a Woolfe's bottle, with three necks at the top and one neck near the bottom (a bottle with two necks at the top only may, however, be used, by having an indiarubber stopper perforated with three holes, through which pass B F, and a syphon reaching to the bottom instead of the tap D. See I.) A bottle 3 feet high by about 5 inches in diameter, as shown by the dotted line, would be much preferable to the one used, which is about 7 inches high by 5 inches diameter, but the former are not at present procurable.

The middle neck of B—E— is used for inserting the sulphide of iron, and should be easily accessible, and fitted with an indiarubber stopper tied down.

The third neck of B is fitted with a tube, as shown at H enlarged. This may be done by drawing out a glass tube to a capillary and sealing the end; the bulb H is then blown out; the tube is then heated at G over the blowpipe flame, while blowing into the other end of the tube until a hole is made, the edges of which are flattened down by the blowpipe; the sealed end is then cut off, leaving a small opening: F is fitted into the neck of B by means of an indiarubber cork pressed down about half an inch, and the cup thus formed filled with melted pitch. The same method is used for the other necks fitted with tubes, and in case of a breakage the stoppers can be removed after warming the neck carefully with a Bunsen flame.

The funnel P in E is kept closed by a glass rod tipped with indiarubber tubing.

The sulphuretted hydrogen branch-pipes for students are made by joining glass T-pieces, as seen enlarged at G. The down pipe T is drawn out to a thick capillary and cut off, and the size of the capillary adjusted by blowing through the other end of the tube, after fitting a glass tube to it with indiarubber tubing, until only a slow stream of air passes when blowing with moderate pressure.

The arrangement of the different bottles can of course be modified by varying the lengths of the connecting-tubes to suit the space available.

In setting up the apparatus care should be taken that fresh acid may be poured into A, fresh sulphide of iron put into B, more water poured into E, and spent acid drawn off through D, without disconnecting any of the parts or moving any of the bottles.

A is filled with dilute hydrochloric acid, one acid to one water.

B. As much mercury is put in B as will fill at least 4 inches of the upright tube.

B. Some small marbles are placed at the bottom of B to prevent D being choked by sulphide of iron, and the rest of the bottle is filled with sulphide of iron.

C contains 3 inches of mercury.

D is filled with cotton-wool.

E is filled with distilled water.

The bulb H in F is not essential.

Taps may be used instead of the clips at TT'.

### *Action.*

The apparatus being set up as described, the tap N being closed, on opening tap A the acid flows gently into B through B, and $H_2S$ gas is generated. As soon as the pressure rises in B the mercury in B is driven back and stops the flow of acid. Should much acid have entered B the pressure may increase until the mercury is depressed to the bottom of I in C, when some gas escapes through K into the draught cupboard. On opening N the gas passes through G into F; thence through D into E, where it is slowly absorbed by the water, which soon becomes saturated. The beaker of solution X is then connected with T by the tube V, and the clip on W opened, when a slow and regular current of $H_2S$ passes until the clip is again replaced on W. Similar beakers may of course be attached to T', T'', &c.

$H_2S$ water may be drawn from E by R as required.

Fresh acid is poured into A as required.

The sulphide of iron in B should be replaced, before it gets low, through E, A being turned off meanwhile.

More water may be added to E through the funnel P, the tap N being turned off before taking out plug Q.

The tap A can be left open, except when putting sulphide of iron into B; and the tap N need only be closed when the apparatus is not required, as the large size of D and the water in E in a great measure prevent the blow off of $H_2S$ through K when a rapid supply of gas is suddenly stopped.

The mercury in the valve B remains quite clear and bright; that in the safety blow-off tube C has become a little blackened after six months' use, but its action is quite unimpaired.

The sulphuretted hydrogen water in E keeps quite clear and bright, and free from any trace of iron.

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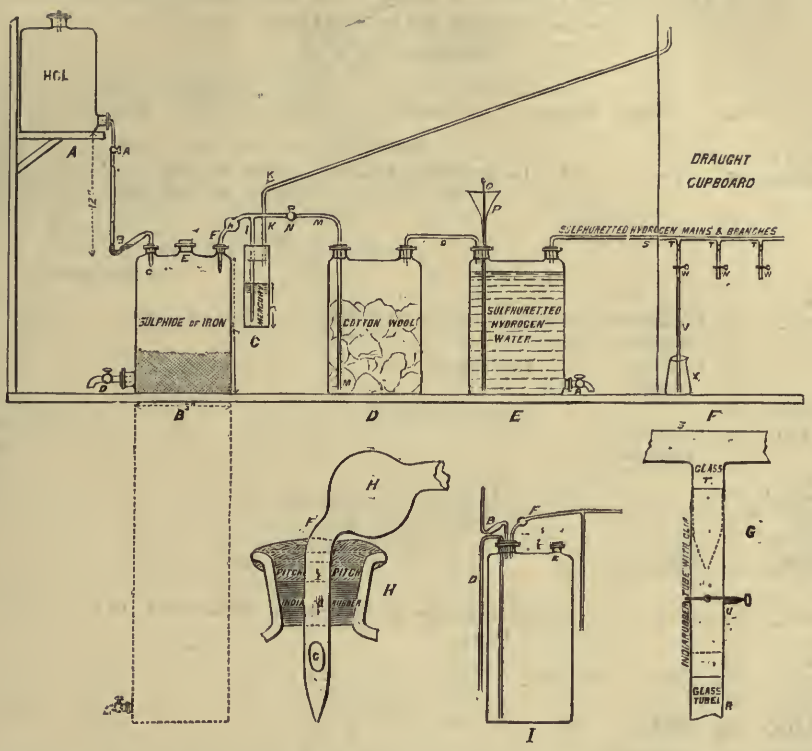
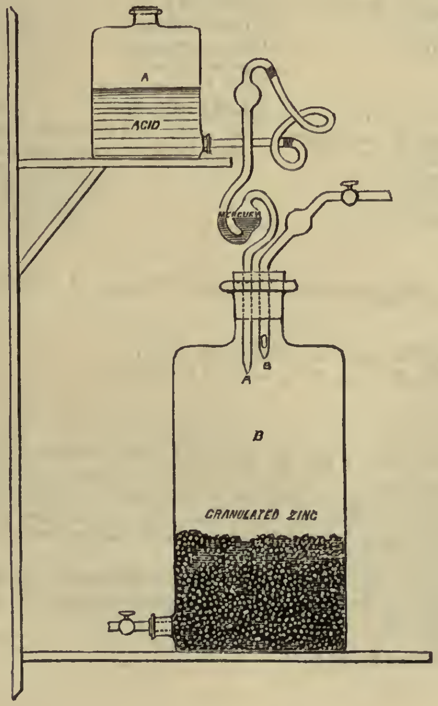
* From the Annual Report of the "School of Mines and Industries of South Australia."

Fig. 1.



The tube F has proved very effectual in preventing the passage of any liquid with the gas, even when the evolution of gas is very rapid. A similar plan has been tried in distilling off the alkaline liquid from a Kjeldahl determination of nitrogen, the end of the tin condenser being drawn out to about 3-16ths of an inch inside diameter, and a slot cut at G (as in H). There was, however, no bulb at H. In working this it was found that the tip at the bottom was always closed by a drop of water, and all the vapour passed through G into the condenser. The distillate from a strongly alkaline solution, kept rapidly boiling, in a test experiment was quite neutral.

Fig. 2.



A modified form of this apparatus has also been tried for generating hydrogen and carbonic acid gas when a constant supply was required for some time, and it was found that the supply could be regulated much more accurately than with the apparatus generally used. Fig. 2 illustrates this apparatus, which requires no further description except that it is well to have the bottle B long and narrow and A short and wide, and the tip of the tube A should be below the tip B. The bottle A can, of course, be raised or lowered as required, being connected to B by indiarubber tubing.

**Radiation of Different Refractory Substances Heated in the Electric Furnace.**—J. Violle.—It was important to know if there occurs in the arc, as Rosetti announced, a temperature notably higher than that of positive carbon. To decide this question I introduced into the arc a fine rod of carbon. This rod was rapidly worn away, becoming hollow on the side facing the cathode, and being coated with a powdery deposit opposite the anode. In a word, it behaves exactly like a metal wire in a galvanoplastic bath, according to the law of Grotthus. On applying to the examination of the cavity in the rod the methods which I had used for studying the extremity of the positive carbon I found that the lustre was the same on the rod as on the positive carbon. I operated on coke, lime, magnesia, zirconia, and chromic oxide, and found that all these different substances present in the furnace exactly the same brilliance and act equally upon the eye and the photographic plate. Thus in an enclosure all parts of which are at an equal temperature all these bodies are in an equilibrium of radiation according to Kirchhoff's law.—*Comptes Rendus*, cxvii., No. 1.

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 44).

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| COBALT. | | | | | | | |
| $CoSO_4(NH_4)_2SO_4+$ $+6H_2O$ | 21 | — | M | Large stumpy prisms. | Some as high as 6th, but generally 3rd order. | No. 21. Within about 8° of *e* in the few cases in which the crystals are elongated. | No. 21. Absorption with single nicol strong. |
| CHROMIUM. | | | | | | | |
| $CrSO_4$ .. .. .. | 22 | Chromous sulphate. | | | | | |
| $Cr_2(SO_4)_3$ .. .. | 23 | Chromic sulphate. | — | Crystalline. | | | |
| $Cr_2(SO_4)_3+5H_2O$.. | 24 | | — | Non-crystalline. | | | |
| $Cr_2(SO_4)_3+15H_2O$ | 25 | Chromic sulphate. | | | | | Green in transmitted light. |
| $2CrSO_4(OH)_4+$ $+Cr_2(OH)_6+5H_2O$ | 26 | | — | | | | |
| *Double Salts.* With sulphates of K, Na, and $(NH_4)$ | — | *See alums.* | — | — | — | — | — |
| CÆSIUM. | | | | | | | |
| $Cs_2SO_4$ .. .. .. | 27 | | R | Prisms with numerous faces. | 2nd order. | *R.L.* to *e*. | |
| $CsHSO_4$.. .. .. | 28 | | R | | | | |
| *Double Salts.* $Cs_2SO_4MgSO_4+$ $+6H_2O$ | 29 | *See Mg.* | M | — | — | — | — |
| With sulphate of Al. | — | *See alums.* | | — | — | — | — |
| IRON. | | | | | | | |
| $FeSO_4+4H_2O$ .. | 30 | Ferrous sulphate. | R<br>M | | | | |
| $FeSO_4+5H_2O$ .. | 31 | Ferrous sulphate. | Tr | | | | |
| $FeSO_4+7H_2O$ .. | 32 | Melanterite or green vitriol. | M | When evaporated on slide generally in rhombs or tabular prisms. | 7th order. | Generally ∥ to a line dividing the obtuse angle of rhomb into two unequal portions. | |
| $Fe_2(SO_4)_3$ .. .. | 33 | Ferric sulphate. | — | In oval and rounded disks, often with radiating fibrous structure and in fibrous patches. | 1st order. | ∥ to axis of elongation. | Extinction coincides with axis of elongation. Decided absorption with single nicol. |

*Remarks.*

*No.* 21.—On heating changes from rose-red to violet: on cooling rose colour returns. Traces of a very oblique bisectrix, apparently positive.

*No.* 22.—Only known in solution.

*No.* 23.—A *red* salt formed by heating No. 24 to 370°. Insoluble in water, alcohol, or acids.

*No.* 24.—A *green* salt. Soluble in alcohol. Formed by boiling No. 25, or by heating it to 100°.

*No.* 25.—A *violet* salt. Insoluble in alcohol.

*No.* 26.—A basic salt.

*Chromates* and *Dichromates*, see K and Na.

*No.* 30.—$FeSO_4$ under ordinary conditions crystallises in the form of No. 32, but it takes the orthorhombic form if its supersaturated solution is touched with a crystal of zinc sulphate, and the triclinic form (No. 31) if a crystal of copper sulphate is placed in a concentrated solution. When a solution of $FeSO_4$ containing free $H_2SO_4$ is allowed to evaporate in a vacuum, No. 32 separates first, then No. 31, and lastly No. 30. When the ferrous sulphate is exposed to the air it is changed into a compound containing ferric sulphate and ferric hydroxide, or a basic ferric sulphate, $Fe_2(SO_4)_3(OH)_3$.

*No.* 33.—Ferric sulphate readily forms basic salts, the composition of which is not positively known. It dissolves slowly in water, and is decomposed by heating into ferric oxide and sulphur trioxide. Columns 5 to 8 is the anhydrous salt dissolved in water and re-crystallised.

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* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

|  | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| IRON. |  |  |  |  |  |  |  |
| $Fe_2(SO_4)_3$ .. .. .. | 34 |  | R | Radiating needle-shaped prisms (see Remarks, Part 3). | Blue of 2nd order. | $\parallel$ to *e*. |  |
| $Fe_2(SO_4)_3+9H_2O$.. | 35 | Coquimbite. | H | Prisms usually with terminal edges replaced. |  |  |  |
| $Fe_2(SO_4)_4+12H_2O$. | 36 | Ferrous ferric sulph. | M | Yellow crystals. |  |  |  |
| $FeS_2O_7$ .. .. .. | 37 | Ferrous disulph. | — | Green microscopic prisms. |  |  |  |
| $FeSO_4(OH)_4+$<br>$+Fe(OH)_6+H_2O$ | 38 | Vitriol ochre. | — | Massive earthy stalactitic. |  |  |  |
| $Fe_2(SO_4)_3+Fe_2$<br>$(SO_4)_2(OH)_2+10H_2O$ | 39 | Copiapite. | H ? | In six-sided crystalline scales. | Red of 2nd order. | $\parallel$ to *e*. | Basal sections give cross on bluish ground in *c.p.l.* |
| $2Fe_2(SO_4)_2(OH)_2+$<br>$+Fe_2SO_4(OH)_4+$<br>$+24H_2O$ | 40 | Fibroferrite. | M ? | In delicate fibres. |  |  |  |
| *Double Salts.* |  |  |  |  |  |  |  |
| $FeSO_4Na_2SO_4+$<br>$+6H_2O$ (see Remarks, Part 3) .. | 41 |  | M | Globulites, spherulites, and radiating fibrous crystals. | 2nd order. | About 45° to longer axis of fibres. | Sometimes has a concentric as well as radiating structure, and resembles chalcedony. |
| $FeSO_4K_2SO_4+6H_2O$ | 42 |  | M | Large tabular crystals. | 7th order and higher. | Variable. | Absorption with single nicol, very strong. |
| $FeSO_4(NH_4)_2SO_4+$<br>$+6H_2O$ | 43 |  | M | Large stout prisms variously terminated. Also in skeleton crystals. | 5th order. | Within a few degrees of $\parallel$ to *e*. | Strong absorption with single nicol. Zonal structure. *In c.p.l.* either an optic axis or a more or less oblique bisectrix emerges. |
| With sulphate of K and $NH_4$ .. .. |  | *See alum.* |  |  |  |  |  |
| POTASSIUM. |  |  |  |  |  |  |  |
| $K_2SO_4$ .. .. .. | 44 | Normal sulphate. | R | Flat prisms elongated in one direction; terminations various. | 2nd order. | Generally $\parallel$, sometimes *R.L.* to *e*. | Relief strong when mounted in balsam; when unmounted faces at angle to glass cover are black. |
| $KHSO_4$ .. .. .. | 45 | Acid sulphate. | M<br>R | (*a*) Six-sided tabular prisms.<br>(*b*) Needle-shaped do., also fibrous.<br>(*c*) Irregular-shaped tabular crystals. | 6th order. | Low angle to *e*. | Absorption with single nicol. Mottled appearance under crossed nicols seldom extinguishing uniformity; unmounted deep black margin; strong relief; shagreened irregular surface marked with black lines. Penetration twins often seen. |

*Remarks.*

*No.* 34.—Is formed by adding No. 32 to boiling $H_2SO_4$.

*No.* 36.—The two sulphates of iron form various double salts, of which this (Roemerite) is one.

*No.* 37.—Is formed by adding iron sulphate to several times its volume of concentrated $H_2SO_4$. It decomposes on contact with water.

*No.* 40.—Pale yellow to white, pearly, or silky.

*No.* 44.—Soluble 1 in 10 in cold and in much smaller quantity of boiling water. Occurs in Apthitalite and Kainite. The difference in appearance of mounted and unmounted specimens is a striking feature, and one useful for identification.

*No.* 45.—Occurs native in the *grotto del solfo*, near Naples, in the form of silky needles. Dissolves readily in water: is decomposed by alcohol into No. 44 and $H_2SO_4$. When 45 is re-crystallised from aq. sol., No. 44 separates out first, then crystals of a salt having composition of $K_2SO_4+KHSO_4$, and finally No. 45 crystallises out.

To be continued).

# ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 47).

### *Photography of the Spectral Region between the Wave-lengths* $231{\cdot}35$ *and* $185{\cdot}2\ \mu\mu$.

A. With ordinary apparatus permeable for the ultra-violet.

*The Photographic Spectral Apparatus, with particular reference to its Optical portion.*—The photography of this spectral region requires an apparatus of great permeability to light. Glass (G. G. Stokes, *Phil. Trans.*, 1852, cxlii., Art. 202), which keeps back most of the ultra-violet rays, is unfit for the prisms and lenses of such an instrument. Calcareous spar is not much better (L. Soret, *Archiv. des Sci. Phys. et Nat.*, lxi., 334 [1878]). Its availability for the ultra-violet ends where the above-named region begins. The only media which can be taken into consideration are quartz (L. Soret, *ibid.*, p. 332, and G. G. Stokes, "On the Change of Refrangibility of Light," *Phil. Trans.*, 1852, Art. 204) and white fluor-spar (W. A. Miller, "On the Phot. Trans. of Various Bodies," *Phil. Trans.*, clii., p. 865 [1862]; A. Cornu, *Archiv. des Sci. Phys. et Nat.*, III. periode, ii., p. 119).

Fluor-spar in its white variety—all other kinds of fluor-spar are coloured and less permeable for the ultra-violet—is more transmissive than quartz; but it has hitherto been applied only in isolated cases on account of its rarity and as it frequently contains defects in crystallisation which imperil the clearness of the image (H. Deslandres, "Spectres des Bandes Ultra-violet des Metalloids avec une faible dispersion," p. 32. Paris: 1888).

In the photography of the ultra-violet region, quartz presents upon the whole greater advantages than any other medium. It yields spectra of faultless definition, and its lower transmissibility—just mentioned—is, according to present experience, not so important as seriously to impair the photographs.

*The Quartz Prism.*—Not every quartz prism is fit for spectral photography. Every prism whose refractive edge runs parallel with the optical axis is unsuitable. The reason lies in the partial superposition of the ordinary and extraordinary ray, and in the circumstance that the photographic result on the extinction of one or other of the two spectra, which is certainly practicable with a Nicol prism, is destroyed by the non-transmissive character of the calc-spar.

The relations are more favourable with a quartz prism, the refractive edge of which is cut at right angles to the optical axis in such a manner that the latter forms equal angles with the refractive planes. If the rays traverse the quartz in the direction of its optical axis they no longer experience the ordinary double refraction, but they undergo circular polarisation, and in so palpable a degree that, *e. g.*, in a prism of 60°, every line of the spectrum is split up into two very nearly adjacent but clearly resolved components. It is plain that such a spectral image must be uncertain even if the lines are mutually isolated, but must be completely obscure in the case of crowded lines. This scission of the lines may indeed be avoided if a system of lines is cancelled by a quarter-wave plate with a Nicol inserted in the emerging ray. But the plate, as it consists of mica (W. A. Miller, *Phil. Trans.*, clii., p. 865 [1862]), is so impervious that it absorbs almost all rays beyond the wave-length $325\ \mu\mu$, and, without considering the inconvenience in photographing occasioned by the impervious nature of the Nicol, it renders any photographic result in the ultra-violet at once impossible.

The only expedient to preserve the image from the disturbing effect of linear and circular polarisation, without interfering with brightness, consists in the use of a double prism (A. Cornu, *Comptes Rendus*, 1885) composed of a lævo- and a dextro-rotatory quartz, each of an equal refractive angle (30°). In preparing such prisms care must be taken that the optical axes of the semi-prisms are placed vertically to their common plane of contact. To avoid the loss of light the semi-prisms may be joined together with glycerin or distilled water; but this is not necessary. Double prisms of this kind, whether single or when several are connected in a circle, give spectra of a faultless definition.

*The Quartz Lens.*—The lenses for the collimator and the camera are best of a plano-convex form. They may either be of a like or of an antagonistic rotatory power. It is, however, essential that the geometric axis has the same direction as the optical axis of the crystal, or, as the opticians call it, are cut at right angles to the axis. Quartz lenses consisting only of one part never double the image. Therefore double biconvex lenses, composed like the double prism just mentioned, of lævo- and dextro-rotatory plano-convex quartz lenses, afford no advantage in spectral photography.

The focal distance of the lenses must be equal, and not exceed 1 metre. If larger, it may easily happen that the aperture of the apparatus is too small. Although lenses of sufficient diameter can be procured without too great difficulty, the aperture of the prism still remains. But quartz prisms with a rather large aperture rank among rarities. Insufficient apertures easily occasion the formation of inflection fringes, which appear on both sides of the brighter lines of the spectrum, and may easily prove serious in interpreting the spectrum.

On the other hand, the focal distance must not be reduced too far, not below ¾ metre, as the spectrum is otherwise too short. An increase of dispersion by the application of several prisms is not to be recommended. With a combination of several double prisms the spectrum appears clearly defined only for a short extent. The greater the number of prisms the shorter is the clearly defined extent. The simultaneous photography of extensive spectral regions should therefore be effected at the outside with a few, but preferably with a single double prism. This applies especially to a general photograph of the ultra-violet region.

It will be understood that the selection of crystals from which prisms and lenses have to be cut has to be effected with great care. Distortions, which are not rare in quartz crystals, make every crystal unfit for use.

As great attention must be given to the nature of the refractive planes, curvatures which, on account of their moderate zize, have in glass prisms no effect on the spectrum, may greatly interfere with the effect of a quartz prism.

Quartz prisms with faulty planes always give an impure image of lines, though less when used singly than when several are associated in a circle. Such a circle is capable of bringing the spectrum into complete confusion.

Excellent prisms and lenses of quartz are made by the optician Bernhard Halle, of Steglitz, near Berlin. As a proof of the excellence of his work, the fact may serve that a circle of nine double prisms supplied to me by Herrn Halle, in which the rays have to traverse thirty-six refractive planes, gives in an extent of 3¼ m.m. all the eighty-five lines which H. C. Vogel's Atlas of the Solar Spectrum shows between the lines H and K.

The moderate sensitiveness of the spectrum to certain defects of the lenses is remarkable. This applies to the centreing and the direction of the optical axis of the crystals. I have been able to use continuously, without disadvantage, a pair of quartz lenses which showed unusual deviations for resolving dense groups of lines.

This circumstance deserves attention the more as the

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

spectrum is very sensitive to all kinds of faults in the quartz.

The adjustment of the prism and the lenses is effected in the same manner as in the spectral apparatus.

(To be continued).

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# ON THE IODOMETRIC DETERMINATION OF THE NITRATES.*

By HIPPOLYTE GRUENER.

(Concluded from p. 42).

*The Decomposition of Nitrates by Antimonious Chloride.*—The failure mentioned above, in attempting to use arsenious oxide to register the action of nitric acid, led to the trial of antimonious chloride as a substitute, inasmuch as this substance is easily oxidisable and less volatile than arsenious chloride in presence of hydrochloric acid. This latter fact is of great importance in the decomposition of a nitrate. The point to be tested was whether the complete decomposition of nitrates by the action of antimonious chloride in hydrochloric acid solution, and the absorption of the nascent oxygen to form antimonic chloride would be secured, so that the antimonious chloride left at the end as compared with the amount taken should give the measure of the nitrate used, according to the equation:—

$$3SbCl_3+2HNO_3+6HCl=3SbCl_5+2NO+4H_2O.$$

Antimony chloride was dissolved in strong hydrochloric acid, and the solution standardised by diluting convenient portions, adding tartaric acid, nearly neutralising with 25 per cent solution of sodium hydrate, treating with excess of hydrogen sodium carbonate and titrating with decinormal solution of iodine in presence of starch, the blue colour being taken as the end reaction.

Known portions of this solution boiled with potassium nitrate for a considerable length of time, then diluted, neutralised, and titrated (all a simple quick process), showed oxidation to the extent of about 90 per cent of the nitrate present. The evidence pointed to the conclusion that the nitrate was broken up, but that the residue failed to register the amount of decomposition. The products of decomposition when passed in a current of carbon dioxide into potassium iodide set free iodine, but had no oxidising effect upon an alkaline solution of arsenious oxide. The conclusion was drawn that nitrosyl chloride was probably given off, which breaking up on contact with water into hydrochloric and nitrous acids exerts no effect upon arsenious oxide in alkaline solution. To see if the nitrosyl chloride was set free in exact measure of the nitric acid lost the following experiments were made.

Into a diminutive retort—made from a pipette shaped like a Liebig's drier, and connected by a sliding joint covered by rubber into a Kjeldahl tube used as a receiver, and so placed that carbon dioxide passing through the apparatus should enter from below—lifting the air before it—was introduced the nitrate, dry, washed down with a few drops of recently boiled water, or, if more liquid was required, with hydrochloric acid, lest the liquid become too dilute. From a burette a definite amount of antimonious chloride solution, somewhat in excess of the nitrate taken, was introduced. The receiver was charged with 0·25 grm. potassium iodide diluted with recently boiled water and was joined to a trap filled with water. After carbon dioxide was passed through the apparatus, for about ten minutes, the solution was warmed on a high boiling bath (103°—107°) to ensure the safety of the retort, to keep the antimony pentachloride from breaking up, to retain the bulk of the acid in the retort, and to prevent mechanical loss. This method of procedure was found entirely satisfactory. After fifteen minutes digestion the receiver and trap were washed out and at once titrated with sodium thiosulphate. The residue in the retort was treated exactly as was the antimonious chloride when it was standardised. The solution here must be kept dilute, lest at the great heat caused by neutralising strong solutions there be action upon the pentachloride on the part of the small amount of tartaric acid now present. The difference between the trichloride left in the retort and the iodine found in the receiver is the measure of trichloride left unoxidised by the nitrate, and by difference we have the measure of the nitrate present. The results are given in Series I. and II. In experiments 1 to 8 the receivers were washed with ordinary distilled water; after that, with water recently boiled.

Series I.

|  | $KNO_3$ taken. Grm. | $KNO_3$ corresponding to I found in receiver. Grm. | Entire $KNO_3$ found. Grm. | Error in $KNO_3$. Grm. | Error in $HNO_3$. Grm. |
|---|---|---|---|---|---|
| 1 | 0·0222 | 0·0020 | 0·0233 | 0·0011+ | 0·0007+ |
| 2 | 0·0336 | 0·0026 | 0·0333 | 0·0003− | 0·0002− |
| 3 | 0·0470 | 0·0045 | 0·0471 | 0·0001+ | 0·0001+ |
| 4 | 0·0553 | 0·0057 | 0·0554 | 0·0001+ | 0·0001+ |
| 5 | 0·0664 | 0·0076 | 0·0679 | 0·0015+ | 0·0009+ |
| 6 | 0·0759 | 0·0082 | 0·0752 | 0·0007− | 0·0004− |
| 7 | 0·0837 | 0·0103 | 0·0841 | 0·0004+ | 0·0002+ |
| 8 | 0·0934 | 0·0113 | 0·0955 | 0·0021+ | 0·0013+ |
| 9 | 0·1034 | 0·0134 | 0·1036 | 0·0002+ | 0·0001+ |
| 10 | 0·0262 | 0·0024 | 0·0259 | 0·0003− | 0·0002− |
| 11 | 0·0127 | 0·0007 | 0·0130 | 0·0003+ | 0·0002+ |
| 12 | 0·0065 | 0·0003 | 0·0067 | 0·0002+ | 0·0001+ |
| 13 | 0·0026 | 0·0001 | 0·0023 | 0·0003− | 0·0002− |
| 14 | 0·1232 | 0·0098 | 0·1227 | 0·0005− | 0·0003− |
| 15 | 0·1540 | 0·0146 | 0·1540 | 0·0000 | 0·0000 |
| 16 | 0·1878 | 0·0210 | 0·1865 | 0·0013− | 0·0008− |

Three more experiments were performed to see if the titration of the iodine set free in the receiver could be accomplished as well in alkaline solution by means of arsenious oxide. For this purpose the solutions from the receivers were poured into a strong solution of sodium bicarbonate, care being taken to prevent loss during effervescence.

Series II.

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 17 | 0·0530 | 0·0052 | 0·0533 | 0·0003+ | 0·0002+ |
| 18 | 0·0547 | 0·0065 | 0·0549 | 0·0002+ | 0·0001+ |
| 19 | 0·0541 | 0·0063 | 0·0537 | 0·0004− | 0·0002− |

The results run from extremes of 0·0021 grm. + to 0·0013 grm. −, with a mean error of 0·00016 grm. +, which tends to emphasize the well-known fact that it is impossible to remove every trace of air from reagents and generator. The operation is quick, taking in all three-quarters of an hour, and requiring very little watching. The experiments given are all that were performed with the apparatus as described, it not having been found necessary to reject a single determination for mechanical mischances.

Neither of the processes described presents in general advantages equal to those of the manganous chloride method to which reference has been made, but under special conditions they may be found useful.

In concluding, I would express my thanks to Professor Gooch for valuable advice and assistance given during the course of the investigation.

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**On the Mercuric Salicylates.**—H. Lajoux and A. Grandval.—The authors have distinguished and examined the normal salicylates and the basic salicylate. The former is a white precipitate, decomposable by heat, and insoluble in water. The basic salicylate is a white powder insoluble in water, alcohol, ether, and chloroform.—*Comptes Rendus*, cxvii., No. 1.

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* *American Journal of Science*, xlvi., July, 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

# THE SPECIFIC HEATS OF THE METALS.*

By JOS. W. RICHARDS, Ph.D.,
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FOR the purpose of showing clearly the field to be covered, I will refer at once to five heads under which the subject will be considered:—

1. Definitions. The range of the subject.
2. Methods.
3. Historical Treatment. The investigators; work done by each.
4. Discussion of the results. Tables, diagrams, formulæ.
5. Theoretical Treatment. Discussion from the chemical and mechanical standpoints.

## I.

The specific heat of a body is the ratio between the amount of heat necessary to increase its temperature 1°, and the amount necessary to increase the temperature of an equal weight of water 1°.

Being a *ratio*, it is, of course, independent of the weights of the substance and water taken, or of the kind of thermometric scale employed, but in order to introduce regularity into these comparisons the weights taken are a kilogrm. or a pound, and the degree either Centigrade or Fahrenheit. Throughout this lecture I shall use the metric unit of weight and the Centigrade scale.

Since the observations on so many substances are to be compared with water as a standard, it will be well to examine our standard carefully, to see if it is invariable. We find that *pure* water is absolutely the same substance at all times, so that no variation can arise from there being two kinds of water; but, examination reveals the fact that the amount of heat required to raise the temperature of a kilo. of water 1° is a different amount at different temperatures. For instance, it takes more heat to heat a kilo. of water from 90° to 91° than from 1° to 2°. Scientists have investigated this matter for fifty years, and it is only quite recently that reliable figures have been obtained showing just to what extent, quantitatively, the specific heat of water varies with the temperature. The French scientist Regnault had found a gradual increase from the freezing-point up, and for this reason the water unit was chosen as the amount of heat required to raise a kilo. of water from 0° to 1°; but since these observations of Regnault have been proven incorrect, the general conclusion now is that the water unit should be considered at from 15° to 16°, at which point the specific heat of water appears to reach a minimum value.

I have just explained how the specific heat of water varies with the temperature at which it is taken. This is also true of all other bodies, so that a complete investigation of the specific heat of any substance would mean the determination of that property at all attainable temperatures, from the lowest to the highest. In the course of such an investigation the substance would in many cases pass from solid to liquid and then to gas, and it would be found to possess different specific heats in these different states. Furthermore, in passing from solid to liquid, or liquid to gas, it would be observed that a large amount of heat is absorbed without any increase of temperature at all. At these points we say that heat is rendered latent in the body. The complete calorific investigation of a body should therefore include the fixing of the temperatures at which such sudden absorptions of heat occur, and the amounts of heat rendered latent.

A new name has thus attached itself to this branch of experimental physics; we now speak of undertaking the "calorific investigation of a substance" in place of the mere determination of its specific heat at ordinary temperatures.

As we shall see more clearly further on, while this subject is properly a branch of physics, yet it treads very close to the foundation ground of chemistry, throwing a side light on many of the conceptions of that science, and tending in many ways to give us chemical theories on a pure mechanical basis.

## II.

Referring to the experimental methods employed in these investigations, we may class them under two heads:—

1. The method of cooling.
2. Calorimetric methods.

The first method may be briefly described as follows:—The substance is made hot, and then placed in a close vessel kept at a constant temperature by a stream of water, and the rate at which it cools carefully observed. A delicate thermometer embedded in the substance is read every five or ten seconds, and the curve of cooling carefully plotted. Since the conditions are such that the amount of heat radiated per second depends only on the temperature of the substance, it follows that the rate at which it will cool will depend directly on the amount of heat stored up in the body, or its calorific capacity. Thus, different substances can be investigated and compared, but it will be readily seen that the method gives only comparative results, and in order to get absolute values, we must take some one substance whose specific heat has been otherwise determined as a standard, and then the values for the other substances can be calculated.

This method was first used by J. T. Mayer, in 1808, and afterwards greatly improved by Dulong and Petit, but the results obtained by it are not considered as accurate as those given by some other methods, and it is not now used to any extent. The complicated formulæ for cooling, which must be used, and the great care required to obtain good results, have also helped to bring the method into disuse.

Under the second head, calorimetric methods, we include all those methods in which the heat capacity of a body is directly measured. This may be accomplished in three ways:—

1. The method of mixtures.
2. The ice calorimeter.
3. The steam calorimeter.

The method of mixtures consists simply in heating up the substance to an accurately-determined temperature, then to immerse it suddenly into a known weight of water, or any fluid whose specific heat is accurately known. From the temperature of the mixture, and the known specific heat of the liquid, the unknown specific heat, or rather the amount of heat given out by the substance under investigation in falling from the high temperature to the temperature of the mixture, becomes known. Of course, in determining the true temperature of the mixture it is necessary to make corrections for heat absorbed by the vessel in which the mixture takes place, &c., but this line would lead to a discussion of calorimetric methods which would be outside the scope of this lecture. But, aside from this difficulty, there are other defects in this method. One of these is the accurate determination of the temperature of the substance as it was dropped into the calorimeter. Even supposing that its temperature while in the air-bath or furnace is accurately determined (a difficult matter for high temperatures) yet, there is a certain fall in temperature during the transfer into the calorimeter, an amount which increases very rapidly with high temperatures. Another defect sometimes mentioned is loss of heat by vaporisation of the water, but this is so small as to be in most cases negligible. The most serious of these defects, the first, has been remedied by the use of the "double method of mixtures," which consists in using two calorimeters and a platinum ball along with the substance being investigated. If the substance and the

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* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

platinum ball are placed in the furnace together, then removed together and dropped simultaneously into the two calorimeters, the amounts of heat given out by each in cooling from the same temperature can be measured, for it can fairly be assumed that the platinum ball is at exactly the same temperature as the other substance at the moment of immersion. But the specific heat of platinum has been investigated with the greatest care, and so from the amount of heat it has given out to the calorimeter we can calculate its temperature at the moment of immersion. In this way the most serious defect of the method of mixtures has been overcome, especially when working at high temperatures. Your lecturer has done considerable work by this double method, with very satisfactory results.

The ice calorimeter measures the heat given out by the substance in cooling to zero by the weight of ice which it melts. Knowing just how much heat is absorbed by one grm. of ice in becoming water, it is necessary only to weigh the amount of water formed to get the heat given up. This calorimeter was first devised and used by Lavoisier and Laplace, and has been greatly improved by Bunsen. As a measurer of heat its principal defect was that all the water produced could not be collected and weighed. Bunsen's improvements largely overcame this error. The other defects incident to its use were principally the loss of heat during transfer to the calorimeter, which can be overcome by the "double method" already explained. All determinations made in this calorimeter depend on the value of the latent heat of water, which is, however, known to a high degree of accuracy.

The steam calorimeter measures the amount of heat absorbed by a body in being heated up to 100° by the amount of steam which it condenses in doing so. For this purpose, the substance at an accurately known temperature is suddenly plunged into a current of dry steam. The weight of water finally collecting on it is determined, and the heat absorbed by the body is the product of this into the latent heat of steam. Like the ice calorimeter, all determinations made in this way depend on this constant, the latent heat. More serious errors, however, are caused by the condensed water falling off the body, and by some of it being carried away mechanically by the steam. Also, since the latent heat of steam is very large, a small error in weighing the water condensed will make a large error in the result. No very exact figures can be expect from this method of investigation.

Before closing this description of methods I might here remark that the latent heat of fusion, a very interesting phenomenon when speaking of the metals, can be determined in several ways. Assuming the melting-point known, we can calculate from the observed variation of the specific heat in the molten state how much heat the *molten* substance would contain at the melting-point; we can in a similar way calculate how much heat the *solid* metal contains at that temperature; the difference between these two quantities will be the latent heat of fusion. Or, we may determine the first quantity directly by taking a large quantity of molten metal and letting it cool gradually to the setting-point. When part is already set, the part which is still fluid and whose temperature is exactly the melting-point is poured out directly into a calorimeter, and the amount of heat in it thus measured directly. The second quantity may also be determined directly by taking a bath of molten metal, letting part set, and then plunging a little spiral of wire of the same metal into the still-fluid part. The heating up of the wire chills a certain quantity of metal into the solid state at this temperature, and the little lump thus formed is dropped into a calorimeter. Or, the latent heat of fusion can be determined by the method of cooling; for while the metal is setting, its temperature remains constant, and from the time which it takes to set, compared with the rate at which the liquid and solid metal cools before and after the setting, the amount of heat evolved during setting can be computed. We need for this, however, to know the value of the specific heat of the metal somewhere in the neighbourhood of its setting-point.

### III.

Historically considered, we may begin by saying that about 1750 it was universally supposed that there was little or no difference in the heat capacity of different kinds of substances, and it was further supposed that solids were converted into liquids by the addition of an insignificant amount of heat when they had once been raised to the melting-point.

Dr. Black, of Edinburgh, was the first to announce correct ideas on these subjects. In his chemical lectures at Glasgow, between 1760 and 1765, he pointed out the great differences in the heat capacities of different substances, and made experiments in his lectures demonstrating the great amount of heat absorbed during the fusion of ice and the vaporisation of water. He determined the latent heat of water to be 140° F. units, equal to 77·8° C. units. A very able assistant of his, Dr. Irvine, made further investigations between 1765 and 1770, and determined the latent heat of fusion of tin, which he called 500°. By this he meant that the heat given out by tin in setting would be sufficient to raise the temperature of 500 times its weight of solid tin 1°, or an equal weight of solid tin 500°. These being Fahrenheit degrees would be equal to 277·7° C. These we might call tin units, and to convert into the ordinary water units we should have to divide by the ratio of the specific heat of water to the specific heat of solid tin at its melting-point. The figure thus reached is not far from that obtained by later observers.

Dr. Crawford was another colleague of Dr. Black, and published in his "Treatise on Heat" the results of many experiments on specific heats. It was said of him, thirty years later, "To this ingenious experimenter we owe some of the most remarkable facts respecting specific heat yet known." He investigated the specific heats of antimony, copper, iron, lead, mercury, tin, and zinc.

Dr. Black called this newly-investigated property of bodies "*capacity for heat*," but before the publication of his and his colleague's results, which was delayed by Dr. Black's great modesty, Professor Wilcke, of Stockholm, who had been working out similar ideas, published the results of some experiments and attached the name "*specific heat*" to this property. Professor Wilcke worked by the method of mixtures, and published values for antimony, bismuth, copper, iron, lead, silver, tin, and zinc.

Dr. Kirwan, in England, made similar experiments, with values for the specific heats of antimony, gold, iron, lead, mercury, and tin.

Lavoisier and Laplace made experiments with their ice calorimeter, the only one of the metals which they seem to have investigated being mercury. We owe to Lavoisier the expression "*latent heat of fusion*," and we find in his writings a wonderfully clear conception of what specific heat really includes, how it increases with temperature and to a different amount in different substances. So clear were his views that an enthusiastic Frenchman exclaims, in 1886, "All work on specific heats since his time has been done on the lines laid down by Lavoisier."

J. T. Mayer, Leslie, and Dalton worked by the method of cooling, but only the latter gives results for the metals, and these appear to be very rough approximations. The method was afterwards greatly improved by Dulong and Petit. Count Rumford and Avogradro can also be included in the list of experimeters in this line, but their results, especially those of Avogadro, were little trustworthy.

Dr. Wm. Irvine, son of Dr. Black's one-time assistant, repeated and extended some of his father's experiments. He determined the latent heat of fusion of bismuth, lead, tin, and zinc.

Rudberg, in 1830, determined the latent heat of fusion of lead and tin by the method of cooling.

Erman made similar experiments in 1830, but the discordance of his results show that his apparatus was not properly constructed or managed.

F. E. Neuman determined in 1831 the specific heats of antimony, bismuth, and zinc, by the method of cooling. De la Rive and Marcet investigated cadmium, cobalt, and molybdenum by the same method.

Dulong and Petit were the first investigators to make any systematic study of the variation of specific heat with the temperature. They determined the specific heat of antimony, copper, iron, mercury, platinum, silver, and zinc, at various temperatures up to 350° C. Their method was that of mixtures. They also determined the specific heats of antimony, bismuth, copper, gold, iron, lead, platinum, silver, tin, and zinc, at ordinary temperatures, by the method of cooling. These scientists were the first to remark that the specific heats of the elements are inversely proportional to their atomic weights—a law which, while not rigidly exact, yet is so nearly true that the slight deviations from it may fairly be ascribed to other causes yet to be investigated. In fact, it will be seen further on, in discussing the theory of specific heat, that this law may be directly deduced from the modern mechanical theory of heat.

Bède in 1855, Byström in 1860, and Naccari in 1877, have made series of experiments in exactly the same manner as Dulong and Petit's first set by the method of mixtures, at temperatures between 100° and 300°. Bède examined antimony, bismuth, copper, iron, lead, tin, and zinc; Byström, iron, platinum, and silver; Naccari, aluminum, antimony, cadmium, copper, iron, lead, nickel, silver, and zinc.

In 1836 Pouillet made a very careful study of platinum, using an air thermometer for recording temperatures and extending his determinations up to 1200° C. He worked with great care, and his results would have been excellent had it not been that a defect in his air thermometer introduced an error of 30° or 40° in his determinations of very high temperatures, and thereby vitiated his results.

A classical set of experiments was made by Regnault by the method of mixtures. Commencing with 1840, he worked for several years in this field, giving us values which are usually regarded as standards. However, whenever he used metals not quite pure for his experiments, he gave figures which have since been revised. He used a steam bath for his upper temperature, so that his figures are really the mean specific heats between 10° or 15° and 98° or 99°, or the true specific heats in the neighbourhood of 55° lo 60°. He investigated twenty-seven of the metals, as follows:—Aluminum, antimony, bismuth, cadmium, cobalt, copper, gold, iron, iridium, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, osmium, palladium, platinum, potassium, rhodium, silver, sodium, thallium, tin, tungsten, and zinc.

Dr. Kopp was a laborious investigator of specific heats. He determined those of many metals and a host of chemical compounds. He used the method of mixtures, but he seems to have worked with unusually small weights of the substances, and from this cause or some others inherent in his apparatus his results on the same substance often varied among themselves 5 per cent, and occasionally even 10 per cent. In all such cases he figures up the average value of all his determinations. Regnault's results for one substance seldom varied over 1 per cent from each other, so that, wherever Kopp's values vary from Regnault's, the latter's deserve the preference. Kopp obtained the mean specific heats between 10° or 20° and 60° or 70°, or the true specific heat at about 35° to 40°. He investigated aluminum, antimony, bismuth, chromium, copper, cadmium, lead, magnesium, platinum, silver, tin, and zinc.

Prof. Bunsen used his modification of the ice calorimeter for determining the mean specific heats of antimony, calcium, cadmium, indium, ruthenium, silver, tin, and zinc, between 0° and 100°, or the true specific heats at about 50° to 55°.

Prof. Mallet determined the specific heat of chemically pure aluminum (used in investigating its atomic weight) between 0° and 100° with Bunsen's ice calorimeter.

Person used Regnault's apparatus and the method of mixtures to determine the specific heats of bismuth, cadmium, lead, tin, and zinc, in the solid and liquid states, from which data he calculated their latent heat of fusion. He also determined the latent heat of fusion of cadmium, silver, and mercury, by the method of cooling.

Dr. W. F. Hillebrand, in 1876, determined the specific heats of cerium, lanthanum, and didymium, by the Bunsen ice calorimeter.

T. S. Humpidge determined the specific heat of beryllium in 1885.

L. Pebal and H. Jahn investigated antimony between −76° and +33°.

Zimmerman and Bluncke both determined the specific heat of uranium.

Nilson and Pettersson investigated germanium and titanium.

Milthaler investigated mercury at different temperatures and derived a formula for the variation of its specific heat with the temperature. Naccari went over the same ground for temperatures between 0° and 250°.

Kunt and Warburg investigated the specific heat of mercury vapour. E. Reynolds determined the specific heat of beryllium, and Mixter and Dana that of zirconium.

Weinhold investigated platinum at high temperatures, using the air pyrometer, but his results are discordant, showing imperfections in his method, so that his results did not supersede those of Pouillet.

More recently J. Violle made a study of platinum up to 1200° C., using the method of mixtures, an air pyrometer, and every refinement possible to ensure accuracy. His determinations are the best we have for this metal, and serve as the basis for calculating the temperature of the ball at the moment of immersion when working by the double method. Violle used platinum in this way for determining the specific heats of gold, iridium, and palladium up to 1200°. He also found the latent heat of fusion of platinum and palladium by determining the amounts of heat in the molten and just-set metal.

Le Verrier (Conservateur des Arts et Metiers) has recently investigated aluminum, copper, lead, silver, tin, and zinc, by the method of mixtures, using the recently-devised Le Chatelier pyrometer to determine temperatures, which it is stated can be done at the very moment of the immersion of the metal in the water of the calorimeter. He finds sharp variations in the specific heats of most of these metals, which no other investigator has seen any indications of, so that his results are very much doubted. Careful and very concordant experiments made by your lecturer on copper, by the double method, have failed to show any indications of variations at points indicated by Le Verrier, so that we must put on Le Verrier the burden of proving his results by repeating his experiments and giving all their details; in short, he must prove his position by further proofs before his results will be seriously considered as true.

Pionchon has done perhaps the most accurate work of recent years in his studies of cobalt, iron, nickel, silver, and tin (1886), and aluminum (1892). He worked by the double method of mixtures, using Violle's formula for calculating the temperature of the platinum. His results are very concordant except in the case of aluminum below 300°, where a variation of 5 per cent between his formula and the experimental results would be possible. Otherwise, he has given complete curves for the specific heats of aluminum, cobalt, iron, nickel, and silver, to 1200°, and tin to 1000°, and determined the latent heats of fusion of aluminum, silver, and tin.

(To be continued.)

## NOTICES OF BOOKS.

*Alkali, &c., Works' Regulation Act*, 1881. Twenty-ninth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1892 presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

THE present report presents few features of an encouraging character. Thirteen additional classes of works have been brought within the purview of the Act, and progress has been made in preventing the discharge of noxious gases. But the light thrown upon the position of our chemical manufactures reveals in some respects a decline. The number of alkali works was in 1890 117, in 1891 113, and last year only 100. Other works included under the provisions of the Act have increased during the same three years from 791 to 810. In some cases a numerical standard is laid down in the Alkali Act limiting the amount of offensive gases which may be allowed to escape. In other cases there is no numerical standard, but it is enacted that "the owner of every work shall use the best practicable means for preventing the discharge into the atmosphere of all noxious gases and of all offensive gases evolved in such work." It may be asked whether this obligation may not be interpreted in too arbitrary a manner?

The total salt consumed in the Leblanc alkali process has progressively declined in the years 1890, 1891, and 1892 from 598,684 tons to 479,869 tons! Even if we take both the Leblanc and the ammonia process together, we find in the same three years a decline from 855,029 to 824,490 tons. It is, however, of interest to note that two new and extensive works on the Leblanc process have been built during the year 1892, *i.e.*, at Irvine and at Felling-on-Tyne. The manufacturers engaged in the ammonia process are meantime continually striving to produce chlorine (for bleaching-powder and chlorate) in connection with that process. Their success would practically involve the closing of the Leblanc works.

A new process is being attempted at Bristol apparently with a fair prospect of success. Mr. Gossage reduces salt-cake with coal without the co-operation of lime in an ordinary black-ash revolver, and after lixiviation he treats the sodium sulphide liquor with carbonic acid from a lime kiln. He makes no tank-waste, but recovers all the sulphur as hydrogen sulphide expelled from the sulphide by the carbonic acid.

At two works an attempt is being made to obtain chlorine by the action of nitric acid upon hydrochloric acid.

The production of sulphate of ammonia has increased from 134,257 tons in 1890 to 149,826 tons in 1892, but the proportion obtained from the shale works has slightly diminished.

There have been during the year 1892 five prosecutions under the Act; all, save one, for non-registration of works.

It is remarked that the enormous chimneys formerly built in the hope of getting rid of the hydrochloric acid gas are now useless, since this gas is the main source of profit. Some of these chimneys have been destroyed; but the loftiest of all, that of St. Rollox, Glasgow, 453 feet in height from the foundation, "still stands as a monument of expensive brickwork."

The principal works most recently brought under the provisions of the Act are those in which sulphuretted hydrogen is or may be given off, and those where hydrochloric acid is made or volatilised.

It is very satisfactory to learn that the escape of sulphuretted hydrogen at first encountered in the recovery of sulphur from tank-waste, by the process of Mr. Alex. M. Chance, of Oldbury, is now overcome, and the presence of this offensive gas is no longer perceived.

The manufacture of arsenious acid has occasioned some difficulty; in one instance the air of the chimney was found to contain 7·40 gr. arsenious acid per cubic foot. The use of wet condensers was found inadmissible; not only was there a waste of arsenic, but the condensing water poisoned the streams. Dry condensers are now used with much better results.

Means are being taken for improving certain manufacturing processes which are indirectly injurious to the health of the workpeople. The Chief Inspector remarks that the most difficult point here is "protecting the workman against himself." The average yearly death rate among the men employed in the alkali manufacture in the Widnes district is 8·51 per 1000, a figure which certainly gives very slender foundations for the sensational articles which have appeared in a certain portion of the press.

The question of coal-smoke, though it does not come within the scope of the Alkali Acts, is being continually forced upon the notice of the inspectors; many people charge upon any chemical works within fifty miles the injury occasioned by the acid evolved by the combustion of coal. The inspectors think that for this evil no practicable remedy has been proposed. It seems to us, however, that the only way of attacking the smoke question is to obtain from every ton of coal consumed its maximum duty, and thus limit the total amount of the nuisance. If we remember that at the lowest estimate three-fourths of the heat generated in our household fires is wasted, we must own that a great reduction both of black smoke and of sulphurous acid is possible. In addition, a reduction of the coal burnt in London to one-fourth its present amount would "draw the fangs" both of the coal merchants' and of the colliers' unions. This, however, is not a question upon which the CHEMICAL NEWS can enlarge.

The air of the underground railways also calls for notice. Mr. Fletcher suggests that each tunnel should be divided longitudinally by a partition of sheet iron running down the middle.

It seems to us that the Alkali Acts are still being worked judiciously, so as to combine the greatest possible protection to the public health and the least practicable interference with the important industrial interests concerned.

*Manual of Bacteriology.* For Practitioners and Students. With especial Reference to Practical Methods. By Dr. S. L. SCHENCK, Professor Extraordinary in the University of Vienna. Translated from the German (by the Author's permission), with an Appendix, by W. R. DAWSON, M.D. Univ. Dublin, late University Travelling Prizeman in Medicine. With 100 Illustrations, partly coloured. London and New York: Longmans, Green, and Co. 8vo., pp. 310. 1893.

DESPITE its increasing importance and the number of minds which have been attracted to it, the study of bacteriology is becoming dangerous. It can scarcely be carried out with thoroughness and success without occasional experiments on living animals. Hence the bestiarians, whose watchfulness is worthy of a better cause, are rising in arms, and denouncing, not alone the authors, but the publishers of such works. The Society for Promoting Christian Knowledge a short time ago brought out an excellent work from the pen of Dr. Percy Frankland entitled "Our Secret Friends and Foes." For this offence the Lord Chief Justice threatens that unless the book is withdrawn he shall at once withdraw himself from the Society. It is a consolation to know that should this threat be effective there are other works—such as the one before us—which cannot thus be suppressed.

Prof. Schenck's work treats firstly of the general morphology and *biology* of micro-organisms. We submit that physiology would be the more fitting term. In this country biology is the entire science of living beings, including morphology, physiology, embryology, and taxonomy. On the Continent it is used in a less definite manner.

The author next takes into consideration preliminary processes, apparatus, and reagents, nutrient materials and methods of cultivation, the examination of microbia under the microscope, the bacteriological analysis of air, of water, of soils, and of putrescent solids; microbia in foods; the examination of pus, of the organs and cavities of the body and their contents, of the digestive tract, of fæces and urine, of the respiratory system, and of the blood.

An Appendix added by the translator examines vaccination against Asiatic cholera, parasitic protozoa, the action of light on microbia, with some recent methods and formulæ.

This book must be warmly recommended, not merely to students, but to practitioners, medical and chemical. It is impossible for the analyst to arrive at satisfactory results in the examination of waters, air, and soils without the aid of bacteriological methods.

*Kelly's Directory of Chemists and Druggists.* This Book includes Manufacturing Chemists, Wholesale Druggists, Drysalters, Patent Medicine Vendors and the Trades connected therewith in England, Scotland, Wales, and most of the Principal Towns in Ireland. Seventh Edition. London: Kelly and Co., Limited.

This very useful work of reference might be no little improved if its classifications were altered. At present it is too comprehensive, or perhaps rather too promiscuous. We scarcely see how the hospitals, herbalists, chiropodists, dentists, and veterinary surgeons can be classed as "connected therewith." It would seem to us that the above callings should come within the scope of a medical directory. Photographers, on the other hand, should, we submit, be transferred to an art directory, where they might appropriately figure along with painters, sculptors, carvers, and engravers.

A useful feature here is that under every town its early closing day, or half-holiday, if one exists, is duly mentioned. This little detail may save commercial travellers no little time and trouble.

Under the heading "Medical Booksellers," there figure the Philanthropic Reform Publishing Offices, an establishment which seems somewhat mysterious. We fear that a publisher who should proceed on philanthropic lines would have the opportunity of doing a large but ruinous business.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 1, July 3, 1893.

**Auto-conduction, a Novel Method of Electrifying Living Beings; Measurement of Electric Fields of Great Frequency.**—A. d'Arsonval.—This paper requires the two accompanying cuts.

**On Chromopyrosulphuric Acid.**—A. Recoura.—The author has recently combined 1 mol. of chromium sulphate respectively with 1, 2, and 3 mols. of sulphuric acid, obtaining thus chromosulphuric, chromodisulphuric, and chromotrisulphuric acids. He has since combined chromium sulphate with 4 and with 5 mols. of sulphuric acid, obtaining novel compounds, with properties entirely different from those of the three above-mentioned acids. The compound with five mols. of sulphuric acid he has named chromopyrosulphuric acid. Its constitution is expressed by the formula $(S_2O_7H)_4Cr_2(OH)_2$. Its solution precipitates all the solutions of metallic salts, even those of potassium, sodium, and ammonium. The precipitate is flocculent and of a greenish white. All these precipitates are quite insoluble.

**Constitution of Colouring-matters of the Rosaniline Group.**—M. Prud'homme and C. Rabaut.—The authors support the view of Rosenstiehl that these colouring-matters are not salts of amines, but ethers of amidic triphenylcarbinol.

**On Cinchonibine.**—E. Jungfleisch and E. Léger.—It appears that chinchonibine is capable of being split up into cinchonifine and apocinchonine. The saline compounds of cinchonibine do not exist. Cinchonibine should disappear from the list of the true isomers of cinchonine. It appears to be a combination of two of these isomers.

**The Metallic Combinations of Gallanilide.**—P. Cazeneuve.—There is here an account of the calcium, barium, zinc, lead, mercury, and copper compounds, the two latter not being regular salts.

**On the Carbohydrates of Helianthus Tuberosus.**—Ch. Tanret.—The tubers, if examined a short time before their complete development, contain saccharose, inuline, pseudo-inuline, inulenine, helianthenine, and synanthrine. At full maturity there appears a small quantity of levulose and glucose.

**Essential Oil of Spike (*Lavandula spica*).**—G. Bouchardat.—The oil of spike consists chiefly of linalol, the camphor of the Laurineæ, eucalyptol, with a little borneol, terpilenol, geraniol, a turpentine, a copahuvene, and traces of undetermined products.

**Heat of Combustion of Coal-gas in relation with its Luminous Power.**—M. Aquilton.—The author thinks that gas may be valued by the calorimetric bomb in preference to the photometer.

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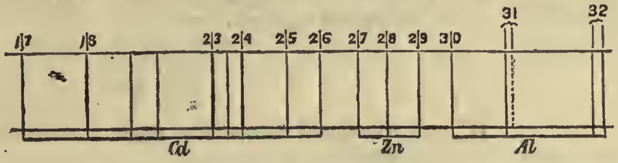
# ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 57).

THE slit-tube of the photographic spectral-apparatus is of the ordinary construction. Only the photographic part of the apparatus differs from well-known instruments, and this only as regards the holder of the dark slide, by which I understand that part of the camera which serves for the reception of the dark slide.

The slide-holder is much more capable of being turned than in the ordinary camera, for the following reason:—Quartz lenses, as their focal lengths decrease considerably with the wave-length, require frequently, in photographing the spectrum, a very unusually inclined position of the photographic plate to the axis of the camera lens. If, *e.g.*, the focal length of the sodium line D (589 $\mu\mu$) is 1000, the focal length for the most refrangible line of aluminium No. 32 (185 $\mu\mu$) is only 806·2 (E. Sarasin, *Archives des Sci. Phys. et Naturelles*, lxi., p. 109, 1878). This oblique position is not constant; it varies with the dispersion and with the proportion of the focal lengths of the collimator and the camera. If the focal length of both is equal (the usual case) the angle between axis and plate, measured on the more refrangible side of both, varies from 22° in a single prism (60°) to about 90° for twelve double prisms (two circles of prisms placed the one behind the other). But the angle is not constant, even for one and the same prism-body. It varies here with the selection of the rays for which the prism is adjusted as at the minimum of deflection, also requirements made for the resolution of single parts of the photograph. Under these circumstances it varies in a single double prism from 28° to 22°. According to a circuit of the angle above named the plate with the dark slide and the slide-holder must be capable of rotation on one of the middle lines of its sensitive side, and have such a position that this medium line forms a parallel to the refractive edge of the prism cutting the optical axis of the camera lens.



### *The Source of Light.*

The purpose of the photograph demands a source of light rich in energetic rays of the shortest wave-lengths.

Only the light of electric discharges fulfils this condition. Hence I had merely the choice between the arc light and the light of sparks. As the latter promised the better result, all my photographs have been produced with spark-light. For its production there was used a Ruhmkorff inductorium arranged for a maximum spark-length of 25 c.m. The primary current was furnished by six Grove elements. A Leyden jar, of 500 square c.m. of external coating, was inserted in the track of the secondary current. In some cases an additional jar was introduced, and even occasionally two more.

For the region of wave-lengths 198·8 $\mu\mu$ to 185·2 $\mu\mu$ only aluminium electrodes are available according to the observations of Stokes (*Phil. Trans.*, clii. p. 606, fig. 1, 1862), and Cornu (*Archiv. des Sci. Phys. et Naturelles*, III. periode, t. ii., p. 125, 1879), and merely for the wave-lengths 230·0 $\mu\mu$ to 198·0 $\mu\mu$, which I could not leave unnoticed, I used electrodes of zinc and cadmium. Zinc and cadmium deserve to be preferred to other metals, on account of the uniform distribution and relatively powerful action of their most refrangible rays.

### *The Photographic Procedure.*

I used dry gelatin plates of my own preparation. Commercial plates are less suitable for the photography of spectra. When it is important to support as far as possible the optical power of the photographic spectral apparatus, where the sharpness of the image is a main condition, and also where a strong contrast in the intensity of the images of the lines is needed (photometry), the commercial plate is inadequate. It does not work intensely enough to assist spectroscopy to the extent of the modern dry plate.

The gelatin plate of my own preparation gives an intense and finely granular image on a ground clear as glass. The emulsion is relatively rich in silver iodide, containing, to 100 parts by weight of silver bromide, 4 to 5 parts of silver iodide. Its preparation is effected exclusively on Eder's method, with silver-oxide ammonia (J. M. Eder, *Ausf. Hand. d. Photographie*, Part III., pp. 208—211, 4th ed., Halle, 1890), which I have used for more than ten years.

For developing the plates I use the soda-pyrogallic developer, and for fixation sodium thiosulphate.

### *The Photographic Proof.*

Before proceeding to treat of photographic proofs it may be remarked that I have long occupied myself in a complete manner with the photography of the ultra-violet region. My chief object was then the development of the graphic portion of the proofs, the most refrangible rays being overlooked. Only now and then, in a transitory manner, I have attempted to photograph the most refrangible lines of aluminium, but without success.

More favourable than with aluminium were the conditions of the most refractive lines of zinc, which precede the above-named aluminium lines in the series of the most striking rays of the ultra-violet. But though I did not here operate unsuccessfully, the image which I obtained was always pale and indecisive.

The most refrangible lines of cadmium, which are still less deflected than most refrangible zinc lines, appeared regularly after a short exposure to light. But in intensity they were decidedly inferior to the neighbouring lines of smaller wave-length of the same spectrum.

In general the wave-length of the cadmium line No. 24 (226·55) formed the limit of my earlier photographs of the ultra-violet.

The above-mentioned most refrangible lines of cadmium, zinc, and aluminium have been marked by Mascart and Soret with numbers, and generally in spectroscopy, where the wave-lengths are not necessary, this system has come into use. I shall use it in what follows. Here follows a list of these lines with the Mascart-Soret characterisation, the wave-lengths as determined by Cornu (*Archives des Sci. Phys. et Nat.*, III. Periode, t. ii., pp. 121—126, 1879), and a design (fig. 1) taken from my own photographs.

(To be continued).

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 55).

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| **POTASSIUM.** | | | | | | | |
| $K_2S_2O_7$ | 46 | Disulphate. | — | In long slender needles. | | | |
| *Double Salts.* | | | | | | | |
| With sulph. of Al, Cr, Mn, Fe, &c. | — | *See alums.* | | | | | |
| With sulph. of Be | — | *See Be.* | | | | | |
| " " Fe | — | *See Fe.* | | | | | |
| " " Mg | — | *See Mg.* | | | | | |
| " " Mn | — | *See Mn.* | | | | | |
| **LITHIUM.** | | | | | | | |
| $Li_2SO_4$ | 47 | | R | | | | |
| $Li_2SO_4+H_2O$ | 48 | | M | | | | |
| $Li_2SO_4+3H_2O$ | 49 | | {H<br>R | (*a*) Six-sided prisms, elongated in one direction; some tabular, some radiated.<br>(*b*) Stars of radiating blades. | White of 7th order. | *R.L.* to *e.* | Some of the crystals show a negative bisectrix in *c.p.l.*, almost all of (*a*) show traces of one. |
| $LiKSO_4$ | 50 | | H | Prisms with pyramidal terminations. Sometimes basal plane truncates the pyramid. | Sometimes so low as to look like an isotropic mineral, sometimes pink of 2nd order. | ∥ to *c.* | Relief good. Margins dark and sharp. Absorption with single nicol. |
| $LiNaSO_4$ | 51 | | H | Spherulitic. | 3rd order. | Various. | Relief good. Sharp dark margins. Slight absorption. |
| $LiNH_4SO_4$ | 52 | | H | Large six-sided micaceous-looking plates. | Generally very low, sometimes as high as blue of 2nd order. | *R.L.* to *e.* | (*n*) Cannot be far from that of Canada balsam. |
| $LiRbSO_4$ | 53 | | H | (*a*) Hexagonal tabular crystals.<br>(*b*) Rectangular four-sided plates.<br>(*c*) Fibrous or stalk-like. | Very feeble. | *R.L.* to *e.* | Outline well defined. |
| **MAGNESIUM.** | | | | | | | |
| $MgSO_4$ | 54 | — | — | | | | |
| $MgSO_4+H_2O$ | 55 | Kieserite. | M | In prisms, or in granular masses. | | | |
| $MgSO_4+6H_2O$ | 56 | — | M | | | | |

### *Remarks.*

*No.* 46.—Is obtained by heating No. 44 in $H_2SO_4$ until the mass fuses quietly. Decomposes on contact with water.

*No.* 48.—$LiHSO_4$ is also known.

*No.* 51.—Some of the spherulites have a radial structure, some have not, and others show a fixed dark cross when revolved between crossed nicols. In the former the cross is very irregular owing to overlapping. Sometimes opaque centres. In *c.p.l.* the spherulites show traces of lemniscates.

*No.* 53.—The hexagonal tables differ from those of $RbSO_4$. Latter are transparent, sharply outlined, and much twinned. 53 are often only translucent, never in my specimens clear or glassy.

*No.* 54.—When this salt is dissolved in $H_2SO_4$ the solution on standing deposits $MgSO_4+H_2SO_4$ in six-sided tables, which soon absorb moisture from the air and decompose.

*No.* 55.—This salt is as difficult of solution in water as gypsum.

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* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

|  | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| MAGNESIUM. |  |  |  |  |  |  |  |
| $MgSO_4+7H_2O$ .. | 57 | Epsom salt. | R | (*a*) Needle-shaped prisms in radiating groups.<br>(*b*) Stout prisms. | (*a*) 2nd order.<br>(*b*) Sometimes as high as 7th order. | (*a*) *R.L.* to *e*.<br>(*b*) Sometimes *R.L.* to *e*, sometimes $\parallel$ to *e*. | Absorption with single nicol. |
| $MgSO_4Na_2SO_4+$ $+6H_2O$ (I have followed Roscoe and Schorlemmer; Fock gives $4H_2O$ for this salt). | 58 | Blödite. | M | (*a*) Crystals like primrose leaves radiating from a centre.<br>(*b*) Elongated irregular shaped prisms radiating from a centre.<br>(*c*) Spherulitic radiating groups. | (*a*) 1st order.<br>(*b*) 7th order.<br>(*c*) Blue of 2nd order. | (*a*) About 45° from axis of quartz wedge.<br>(*b*) High angle to *e*.<br>(*c*) About *R.L.* to *Q.W.* | Absorption with single nicol. |
| $MgSO_4K_2SO_4+$ $+6H_2O$ | 59 |  | M | Large irregular crystals. | 7th order, sometimes higher. | — | Absorption here and there. Internal structure often not homogeneous, giving dusty appearance. |
| $MgSO_4(NH_4)_2SO_4+$ $+6H_2O$ | 60 |  | M | (*a*) Prisms with complex terminations elongated in one direction.<br>(*b*) Stumpy prisms, not elongated. | (*a*) 3rd order.<br>(*b*) 7th order. | (*a*) Within 8° or 9° of $\parallel$ to *e*. | Strong absorption with single nicol zonal structure. (*a*) Extinction 5° to 8° from (*e*). In *c.p.l.* an optical axis emerges from (*a*). |
| $MgSO_4Cs_2SO_4+$ $+6H_2O$ | 61 |  | M | Large tabular crystals; shapes varied and irregular, rarely well formed prisms. | Sometimes as high as 6th order. | — | Absorption with single nicol. |
| $MgSO_4Rb_2SO_4+$ $+6H_2O$ | 62 |  | M | Generally in rhombs, sometimes with two corners truncated. | 5th order. | High angle to *e* when crystal is elongated. | Absorption with single nicol. |
| MANGANESE. |  |  |  |  |  |  |  |
| $MnSO_4+H_2O$ .. | 63 |  | M |  |  |  |  |
| $MnSO_4+4H_2O$ .. | 64 |  | R<br>M |  |  |  |  |
| $MnSO_4+5H_2O$ .. | 65 |  |  | A platy mass of felted blade-like crystals, sometimes radiated, sometimes like the shafts and barbs of a bird's wing. | 7th order. | High angle to *e*. | Strong absorption with single nicol. Some crystals show a negative bisectrix. |
| $MnSO_4+7H_2O$ .. | 66 |  | R<br>M |  |  |  |  |

### *Remarks.*

*No.* 57.—At the ordinary temperature 100 parts of water dissolve 125 of salt. Epsom salt on heating melts in its water of crystallisation, and loses six molecules of water at 150°. The last molecule is not driven off until 200° is reached. The prisms are usually six-sided, with complex to rounded terminations. 57 (*b*) commonly contain liquid cavities with bubbles; also endo-prisms. There is conclusive evidence that the latter are not negative crystals.

*No.* 60.—Liquid cavities with bubbles very common. Often arranged in zones.

*No.* 61.—Liquid cavities with bubbles rather numerous.

*No.* 62.—If the concentrated solution of manganous sulphate is allowed to evaporate *below* 6°, rhombic crystals of No. 66. are deposited. Between 7° and 20° (viz., at the ordinary temperature) crystals of No. 65 are formed. Between 20° and 30° No. 64 is deposited (Roscoe calls them "quadratic"); at the same time a crystalline crust containing $3H_2O$ is formed.

When the hydrates are heated to 200°, or their concentrated solution is boiled, the anhydrous salt $MnSO_4$ is deposited in a reddish yellow powder. It decomposes at a bright red heat. Manganous sulph. is insoluble in absolute alcohol, but it removes a portion of the water from the hydrates.

(To be continued).

## A NEW METHOD FOR THE PRODUCTION OF PURE PHOSPHORIC ACID.

By **H. N. WARREN**, Research Analyst.

A soluble phosphate, preferably sodium phosphate, is introduced into a solution of copper sulphate; and the insoluble copper phosphate thus produced, after washing, is dissolved in solution of phosphoric acid: the solution thus obtained is brought into suitable tanks, into which is placed, in order to retain the strength of solution, a further quantity of copper phosphate enclosed in porous bags. The solution is next electrolysed with medium voltage, using platinum electrodes; a pure and very dense copper is then thrown down. This, if regulated in accordance with the intensity of the current, may be obtained as a crystalline precipitate. The liquid phosphoric acid being electrolysed, with additional quantity of copper phosphate, until the required density is obtained, a large quantity of pharmaceutical acid of 1·75 sp. gr. may thus be obtained in a short space of time.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

## REMARK ON RED PHOSPHORUS.

By W. MUTHMANN.

Herr Ratgers has recently contributed a memoir to the *Zeitschrift für Anorganishe Chemie* (iii., 399) in which he shows that the red modification of phosphorus is not amorphous, but crystalline, and that consequently the name "amorphous phosphorus" should be abandoned in favour of "red phosphorus." This latter name is already in use, and is *e. g.* exclusively employed by Rammelsberg in his "Lehrbuch der Krystallographischen Chemie," and by Michaelis in Graham Otto's "Lehrbuch."

Meanwhile I should remark that red phosphorus can be easily obtained also in an amorphous state, and that the red phosphorus of commerce is often a mixture of the amorphous and the crystalline products. If we heat ordinary phosphorus in a sealed glass tube for twenty-four hours to 230°, in an atmosphere of carbonic acid, the resulting product is chiefly amorphous, and contains crystalline parts only here and there.

In my experiment I had placed the tube vertically in the air-bath, and I observed that in its upper part there was deposited an exclusively amorphous product in the form of a crust adhering to the glass, and occasionally also in the form of drops. This red phosphorus can likewise be distinguished externally from the crystalline form. It has a lighter (orange-red) colour, whilst the crystalline kind has a violet surface colour; it is also very brittle, and can be easily ground to a very fine powder.

For examination in polarised light a specimen of the powder was extracted five times with carbon disulphide in order to remove colourless phosphorus, placed on an object-glass, moistened with α-bromnaphthaline (index of refraction for Na light 1·658), and rubbed up with a covering-glass. The several particles transmitted light with a fine orange-red or yellowish-red colour; they proved perfectly isotropic; the fracture was distinctly conchoidal. Hence the substance displays all the properties of an amorphous substance.

It was otherwise different with the portion of the phosphorus remaining in the lower part of the tube. It had a darker colour than the sublimed portion, and, after levigation and extraction with carbon disulphide, it had exactly the properties which Retgers observed in the commercial product. It was therefore a finely crystalline aggregate.

The portion formed in the upper part of the tube, being produced by sublimation, was beyond doubt purer than the residue just described. It seems hence that the crystallisable property of red phosphorus is increased by the impurities generally present, consisting chiefly of traces of arsenic.

As for the red phosphorus of commerce it is, as Retgers correctly remarks, almost always finely crystalline; but in one of three samples which came under my examination I found particles of an orange colour and a conchoidal fracture, which on microscopic examination proved to be amorphous.

Moreover the above results are not novel, since MM. Troost and Hautefeuille (*Comptes Rendus*, lxxviii., p. 748) have some time ago reached the same conclusions. They observed that red phosphorus has a darker colour as the specific gravity is higher. The lower the heat of combustion the higher was the temperature at which it was prepared. On heating very pure ordinary phosphorus to 265° for 650 hours, the above-named authors obtained a splendid red mass of a vitreous fracture and a sp. gr. of 2·148. This is evidently the same amorphous substance which was formed in my experiment from the sublimed phosphorus.

Troost and Hautefeuille also obtained red phosphorus in distinct ruby-coloured crystals, of sp. gr. 2·34, by heating ordinary phosphorus to 580°.—*Zeitschrift für Anorganische Chemie*, iv., p. 303.

## DETERMINATION OF THE HYDROCYANIC, HYDROSULPHOCYANIC, AND HYDROCHLORIC ACIDS.

By P. L. JUMEAU.

The scanty information which we possess on the determination of the sulphocyanides and cyanides in presence of chlorides has induced us to study this question.

### *Determination of Hydrosulphocyanic Acid in presence of Chlorides and Cyanides.*

We cannot attempt to determine hydrosulphocyanic acid directly with silver nitrate in presence of cyanides or chlorides, the acids CHNS, HCl, and HCy being equally precipitable by this reagent, and their precipitates behaving identically with reagents, as they are entirely soluble in ammonia and completely insoluble in dilute nitric acid.

It has been proposed to determine it by oxidising a known weight of the substance in solution by potassium permanganate, and precipitating the sulphuric acid produced with barium chloride and weighing the barium sulphate. The proportion of sulphocyanide or of hydrosulphocyanic acid is deduced from the weight, 100 parts $SO_4Ba = 50{\cdot}643$ CNSH.

When the solution contains sulphates along with sulphocyanides it is necessary first to determine the pre-existing sulphuric acid by precipitating a known volume of the liquid with $BaCl_2$. A second precipitation is then effected in an equal volume of the liquid after oxidation, and the excess of $SO_4Ba$ found in the second experiment enables us to calculate the hydrosulphocyanic acid.

We thought that the same end might be reached by the result of standard solutions. We prepare a liquid containing about 10 grms. $NH_4CNS$ per litre, and determine volumetrically its exact value with silver nitrate in an acid medium ($NO_3H$) in presence of a ferric salt, or by weighing the silver sulphocyanide: 100 parts CNSAg correspond to 45·783 ammonium sulphocyanide or 35·542 hydrosulphocyanic acid.

On the other hand, we dissolve about 8 grms. permanganate in a litre of water. We take 5 c.c. of the standard solution of ammonium sulphocyanide, and dilute with water to make up nearly 100 c.c.; we add 10 c.c. pure $SO_4H_2$, and then, drop by drop, the permanganate solution contained in a burette. The permanganate is immediately decolourised. There is formed hydrocyanic acid, which is partly set free at the same time as the sulphur is converted into sulphuric acid. As soon as a drop of permanganate is in excess the mixture takes a bright rose tint, which remains for a long time. We note the number of c.c. added; then it is easy to calculate how much permanganate corresponds to the sulphocyanide or the sulphocyanic acid.

When once its standard is known the permanganate liquor may serve for a great number of determinations. It is sufficient to dissolve 1 grm. or more of the substance to be examined, according to its supposed proportion of CNSH, make up the volume of the solution to 100 c.c., add 10 c.c. $SO_4H_2$, and then the permanganate drop by drop until a permanent rose tint appears.

### *Hydrosulphocyanic and Sulphuric Acids.*

If for the 10 c.c. $SO_4H_2$ we substitute HCl we may, when the determination is completed, verify the number found by weight; it is sufficient to expel by heat the chief part of the acid, dilute with water, and precipitate the sulphuric acid produced as barium sulphate. The results should agree perfectly; if not, the substance in question must contain sulphates as well as sulphocyanides.

### *Hydrocyanic or Hydrochloric and Hydrosulphocyanic Acid.*

When it is required to determine at once the acids CNSH and HCy in the absence of chlorides, or CNSH and HCy in the absence of cyanides, we make a first determination of the two acids by precipitating them together with silver nitrate, and note the weight of the precipitate. On the other hand we determine, in another portion of the solution, the CNSH as above directed, and transform the result into silver cyanide: 100 parts CNSH = 281·35 NCyS; the figure found, subtracted from the first result, gives the weight of the silver cyanide or chloride, as the case may be, and consequently the proportion of HCy or HCl.

We may also take merely one portion of the solution under analysis, precipitating the two acids together by silver nitrate, weighing the precipitate, re-dissolving it in ammonia with the aid of heat, diluting with water to prevent the formation of salts of argent-ammonium, and precipitating the silver with an excess of HCl. The silver chloride is filtered off, washed, and the CNSH is determined in the filtrate and washings by means of permanganate as above directed (but without the addition of $SO_4H_2$).

We thus find rapidly and accurately the weight of the silver sulphocyanide and the other acid by difference. When the titration of CNSH is completed we may precipitate the sulphuric acid produced, and verify by weight the figure obtained.

### *Hydrosulphocyanic, Hydrocyanic, and Hydrochloric Acids.*

If it is required to determine the three acids in a mixture, we begin by separating them from the other acids and bases which may accompany them by precipitating all three by silver nitrate in a liquid acidified with nitric acid, and weigh the mixture—

$$AgCyS + AgCy + AgCl.$$

We re-dissolve the precipitate in ammonia, and determine the hydrosulphonic acid as already directed—at first volumetrically by HCl in an acid medium, and then by weighing the $SO_4Ba$: 100 parts of barium sulphate correspond to 71·244 silver sulphocyanide.

*AgCy.*—After a preliminary research has indicated the presence of a larger or smaller quantity of cyanides* we precipitate a considerable volume of the substance in question, and precipitate with silver nitrate, so that the precipitate AgCNS + AgCy + AgCl may contain a noteworthy quantity of silver cyanide.

Of this precipitate we take at most 1 grm., and determine in it the nitrogen.

Contrary to the opinion of certain authors the cyanides yield the totality of their nitrogen by the Kjeldahl process, modified as follows:—The weighed precipitate is placed in a platinum capsule of 10 c.m. in width and 5 c.m. in depth. We cover it with 15 c.c. of Nordhausen sulphuric acid, add 0·750 Hg, place upon the capsule a funnel which fits its sides, and heat nearly to the point of ebullition of the acid. The solution is effected rapidly; we still keep up a little heat, wash the funnel when cool externally and internally, and transfer the liquid into a like flask. The capsule is carefully washed, and the entire volume made up to about 300 c.c.

The flask is closed with a caoutchouc stopper having two perforations. The one receives a tube funnel passing to the bottom of the flask; the other aperture admits the end of an ascending worm, or more simply a tube, upon which two bulbs have been blown at slight distances, and which is then twice bent at right angles. The free extremity plunges into 10 c.c. of dilute standard sulphuric acid.

We pour in through the funnel tube 85 c.c. of soda-lye of sp. gr. 1·31, then 5 c.c. of a saturated solution of sodium sulphide, and connect the tube with a hydrogen apparatus.

By operating thus we escape any loss of ammonia on the saturation of the acid by the soda. It is merely requisite to distil in order to drive the ammonia into the standard acid (causing the current of hydrogen to pass which regulates the ebullition and sweeps out the apparatus), and to titrate the distillate.

From the figure found it is proper to deduct the ammonia introduced by the reagents. To this end we perform a second distillation with equal volumes of the reagents employed: 15 c.c. Nordhausen sulphuric acid, 300 c.c. water, saturated as above with 85 c.c. soda-lye and 5 c.c. sodium sulphide. This correction must never be neglected.

When the correction has been made the remainder represents the nitrogen of the silver cyanide and of the sulphocyanide. The weight of the latter being already known, we can calculate its proportion of nitrogen: 100 parts AgCNS = 8·4337 N. On deducting from the nitrogen determined the nitrogen of the sulphocyanide, the remainder is the nitrogen of the silver cyanide, and on multiplying it by 10·4477 we have the proportion of the latter.

*AgCl.*—On deducting from the weight of the precipitate analysed AgCy + AgCNS as already obtained, the difference gives AgCl.

If we wish to determine the chlorine directly instead of finding it by difference, we first determine in the solution of the substance CNSH, as already directed in a liquid acidified with $SO_4H_2$; we then expel the hydrocyanic acid produced by the reaction, and the hydrocyanic acid of the cyanides, by ebullition in presence of zinc, and in the residue we precipitate chlorine with silver nitrate. By this process we may determine the three acids. It is sufficient to precipitate another portion of the solution in question with silver nitrate. On deducting from the total weight the acids CNSH and HCl calculated as salts of silver, the difference will be AgCy.—*Bull. de la Soc. Chim. de Paris*, vols. ix.—x., p. 346.

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**On the Saturation of the Nitrogen of Nicotin, and on an Acetylnicotine.**—A. Etard.—Nicotin is active by means of carbon. This activity persists in the hydrides, and disappears in isodipyridine. It yields both a dihydride and a hexahydride. On pyrogenation there is an almost exclusive formation of β-propylpyridine. Nicotin combines with acetic anhydride by simple addition, $C_{10}H_{14}N_2(C_2H_3O)_2O$.—*Comptes Rendus*, cxvii., No. 3.

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* If we search for cyanides by the formation of Prussian blue, it must be observed that the precipitation is incomplete in presence of sulphocyanides. Small quantities are not detected by this method.

## THE DETERMINATION OF PHOSPHORUS IN VEGETABLE SOILS.

By ADOLPHE CARNOT.

The detection of phosphorus in vegetable soils may be simplified by means analogous to those which the author has already indicated for the determination of phosphorus in steels (*Comptes Rendus*, Jan. 16th, 1893). In the first place the method of destroying the carboniferous compound by means of concentrated nitric acid and chromic acid, though very suitable for steels, does not suffice for vegetable soils, especially if humus is present in important quantity. A preliminary roasting is then required for eliminating the chief part of the organic substances.

Secondly, the use of sulphuric acid may occasion great difficulties with soils on account of the formation of a larger or smaller quantity of sparingly soluble calcium sulphate. But I have found that we may here dispense with the isolation of silica by employing subsequently, as in the case of steels, the method of double precipitation of the phospho-molybdate, a method to be recommended on other grounds, especially because it enables us to obtain a final precipitate of a quite definite composition. I have ascertained, in fact, that the determination of phosphoric acid is not altered by more than half a hundredth if we introduce sodium silicate into the nitric liquid before the addition of the nitro-molybdate.

The detection of phosphoric acid in vegetable soils may be performed in the following manner:—

We take 10 grms. of the soil sifted and dried at 100°. If it contains much organic matter it is destroyed as well as possible by roasting at a very moderate temperature, which would be useless for soils poor in humus or for specimens of sub-soil.

We first pour into the capsule a little water to steep the soil and then nitric acid in small quantities until no further effervescence is produced. When this point has been reached we add further 10 c.c. of the same acid and allow it to remain for two hours on the water-bath or the sand-bath at about 100°, stirring from time to time with a platinum spatula or a glass rod, and adding, if needful, a little acid to hinder the substance from drying up.

It is then taken up with hot water, filtered, and the insoluble residue is washed. The liquid is then concentrated, and when its volume is reduced to about 50 c.c. we add 5 c.c. of concentrated nitric acid and about ½ grm. of chromic acid in crystals. Then placing a small funnel over the vessel to cause the condensed vapours to fall back, we heat it to ebullition for half an hour to complete the destruction of the organic matter.

We add to the liquid 5 grms. of ammonium nitrate in order to facilitate the precipitation of the phosphoric acid, and then 50 c.c. of the nitric solution of ammonium molybdate. The solution is prepared by dissolving in water 150 grms. of crystalline ammonium molybdate, diluting to 1 litre, then pouring into it one litre of nitric acid of specific gravity 1·20, leaving the whole for three or four days at the temperature of 60°, separating the clear liquid and using only the clear liquid.

It is heated to about 100° for an hour on the water-bath or the sand-bath. In this time the precipitation is completely effected by reason of the large proportion of the molybdic solution and the ammonium nitrate.

After having allowed the precipitate to subside the clear liquid is decanted off, there is put in the beaker a little water acidified with $\frac{1}{20}$ of its volume of the molybdic solution. It is shaken up, allowed to subside, and again decanted twice, causing the liquid to pass through a small flat filter which retains the particles of precipitate carried away in washing.

The precipitate is then treated in the flask and on the filter with 30 c.c. of ammonia mixed with an equal volume of hot water. The washing is completed with 50 c.c. of hot water rendered slightly ammoniacal, and the entire liquid is received in a small flask and suffered to cool.

We pour into it dilute nitric acid until the ammoniacal liquid is neutralised, taking care to proceed slowly and to cool the flask, if necessary, to prevent the temperature from rising above 40°. When the yellow precipitate of phospho-molybdate is no longer re-dissolved on agitating the liquid, that is to say when the ammoniacal liquid has been neutralised, we add further 3 c.c. of pure nitric acid mixed with 4 to 5 c.c. of water and as much molybdic solution. It is left at rest for two hours at 40°, then the precipitate and the liquid are poured upon a tared filter. We complete the washing with a little water acidified with 1 per cent of nitric acid, then with a little water, using the filter pump. It is dried in the stove at 100° and weighed at once.

The weight found if multiplied by the coefficient 0·0373 gives the proportion of phosphoric acid contained in the 10 grms. of soil submitted to analysis.—*Bull. de la Soc. Chim. de Paris.*

## A CRYSTALLINE CHROMIUM TUNGSTATE.

By EDGAR F. SMITH and HERMAN L. DIECK.

Potassium bichromate was brought together with an equivalent amount of pure tungstic oxide. Heat was applied to the mixture; fusion followed and the mass was held in this condition until the evolution of gas bubbles ceased. The temperature was never higher than necessary to maintain a liquid condition of the mixture. After cooling, the fused mass was treated with water until the latter ceased to dissolve anything. Sodium hydroxide and ammonium hydroxide were next employed for washing purposes, and these finally displaced by pure distilled water. The well-washed substance was carefully dried at 100°. It showed a dark brown colour, and when examined under the microscope revealed the presence of acicular, brown-coloured crystals of orthorhombic outline: associated with these were green-coloured crystals, which were apparently of the same crystallographic system. This mixture was exposed to the action of aqua regia for an hour; it was then filtered, washed, and dried. A re-examination of the brown residue showed that the green crystals had been removed and that the brown-coloured body alone remained. It had been unaffected by the acid. Two weighed portions of the mixed crystals were treated with aqua regia, the acid solutions evaporated, the residues dissolved in water, and the aqueous solutions treated with ammonium hydroxide. Chromium hydroxide was precipitated. In the one case the ignited oxide equalled 2·89 per cent and in the other 2·92 per cent of the original mixture. A sufficient quantity of pure brown crystals was prepared for analysis. We first endeavoured to effect their decomposition by fusion with sodium carbonate and sulphur. Several attempts demonstrated that this course offered little chance of a satisfactory analysis. Digestion with hydrofluoric acid gave a poor result; the acid failed to completely decompose the material. Portions of the substance were next ignited in a current of hydrogen, the residue then oxidised with aqua regia, evaporated to dryness, and treated with ammonium hydroxide. Considerable tungsten was removed in this manner, but much remained with the chromium, from which it seemed almost impossible to free it. The mixture of tungstic and chromium oxides was ignited a second time in hydrogen and again treated with aqua regia. This operation was repeated until no more tungsten could be extracted. Combining the separate portions of tungstic oxide, their total quantity gave 88·37 per cent $WO_3$. The chromium oxide, previously associated with this amount of tungstic oxide, equalled after careful purification 11·75 per cent. This method of analysis having proved tedious and time-consuming, we determined to try fluxing the brown coloured material with a mixture of pure sodium carbonate and potassium nitrate, as we had previously satisfied ourselves that it did not contain the alkali metals. The fusion was taken up with water, acidulated with hydrochloric acid, and evaporated to dryness. Tungstic acid separated; the residue was moistened with acid and again evaporated. It was then digested with acid and left pure tungsten trioxide, which was filtered, washed, and weighed. It equalled 88·08 per cent. The chromium oxide in the filtrate, after precipitation and purification, equalled 12·10 per cent. Upon repeating this course with new portions of the substance we obtained results that agreed with those just given, so that we feel satisfied that they represent the true composition of the brown crystals. Taking the mean of the percentages of the two analyses given above as a basis of calculation we deduce as the most probable ratio, $1Cr_2O_3,5WO_3$ or $Cr_2O_3.5WO_3$. The theoretical requirements of this formula are:

| | Per cent. |
|---|---|
| $WO_3$ .. .. .. .. .. .. | 88·40 |
| $Cr_2O_3$ .. .. .. .. .. .. | 11·59 |

| | Per cent found. | |
|---|---|---|
| $WO_3$ .. .. .. .. | 88·37 | 88·08 |
| $Cr_2O_3$ .. .. .. .. | 11·75 | 12·10 |

Tungstates of chromium that exist ("Fremy's Encyclopedie Chimique," iii., 166) are hydrous and have been prepared by double decomposition in the wet way. The salt we describe is, so far as we can ascertain, the first of its class.—*Journ. Amer. Chem. Soc.*, xv., No. 3.

## THE SPECIFIC HEATS OF THE METALS.*

By JOS. W. RICHARDS, Ph.D.,
Instructor in Metallurgy, &c., in Lehigh University.

(Continued from p. 60).

An exactly similar set of experiments was made by your lecturer on aluminum, up to 600°, with a determination of its latent heat of fusion. In connection with Prof. B. W. Frazier, of our University, a similar set of experiments is now in progress with copper, the result of which will give the curve for its specific heat to the melting point, its latent heat of fusion, and the specific heat of molten copper. The approximate values so far found are given in discussing copper. The calorimeters and apparatus used by Professor Frazier and myself are shown in the accompanying cuts. Fig. 1 shows a section of the calorimeter. The outer box is walnut, the calorimeter proper is of thin brass, tightly covered, packed in with cotton. The stirrer is of wire mesh, fitting closely to the walls, and provided with a glass rod for a handle. (Wooden rods warped and worked stiffly.) The thermometers are standard Baudin, graduated to 0·02° and easily read with a lens to 0·0025°. The calorimeter is charged with about 300 grms. of water, and using a platinum ball of 52 grms., the rise in temperature is approximately 0·5° for every 100° fall of the platinum ball. The corrections for losses of heat to the calorimeter during the experiment are made by a system worked out by us, which gives most satisfactory results, but which cannot be described in the limits of this lecture. Suffice it to say, that the probable errors in the calorimeters themselves are within 0·1 per cent.

Fig. 2 shows the apparatus for containing the metals in the furnace. It is a piece of fire-brick, cut as indicated, and with two smooth French annealing cups fastened into the holes. In operation, the platinum is put in one side, the other metal in the other, and the crucibles covered by porcelain lids connected by a stout platinum wire. The whole is then heated several hours at the desired temperature. Everything being ready, the two calorimeters are brought into the furnace room, opened to receive the balls, the brick withdrawn from the furnace, the lids lifted off by the platinum wire, and then by inclining the brick between 45° and 90° to one side one ball is dropped into its calorimeter, and by inclining the brick to the other side the other is dropped into its. The stoppers are replaced, the calorimeters carried to their room and readings taken for five minutes. In order to correct all possible errors, a full experiment consists of

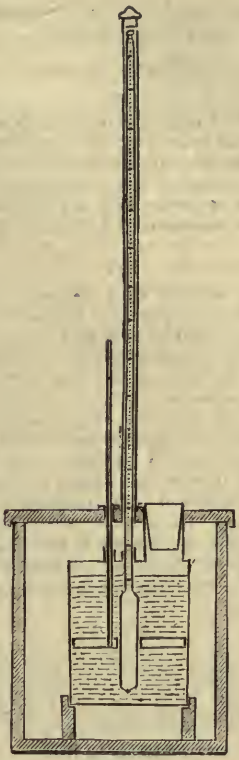

Fig. 1.

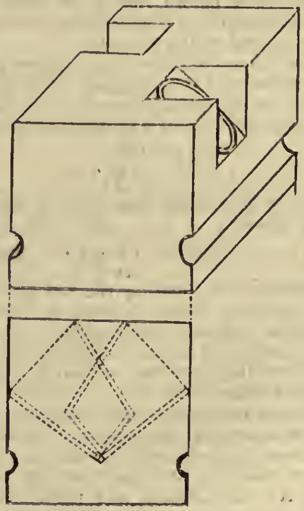

Fig. 2.

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* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

two separate ones made as nearly as possible at the same temperature, but with every condition which could affect the result reversed; these are:

1. The position in the furnace.
2. The position in the brick.
3. The order of dropping out of the brick.
4. The calorimeter into which it is dropped.

With these precautions, we have not rested satisfied until we have attained to a maximum difference between corresponding experiments of *less* than one per cent, and a deviation from the mean of *less* than 0·5 per cent.

## IV.

In general we may say that the only factor we really find out in investigating specific heats by the method of mixtures is the amount of heat given out by the substance in cooling through a certain range of temperature. The lower temperature is that of the calorimeter, which usually varies between 15° and 25°, while the upper temperature varies at will. If the results obtained for any one substance are plotted on a diagram, taking the range of temperatures as abscissæ and the heat given out as ordinates, it is at once found for most metals that a straight line will not pass through the points. The heat given out increases in greater proportion than the temperature, giving a curve which is convex towards the axis of abscissæ, gradually getting steeper and steeper. The formula for such a curve must then be of this nature:—

$$Q=\alpha t+\beta t^2 \qquad (1)$$

in which Q represents the quantity of heat given out to zero, and $t$ any temperature. If a curve of this nature does not rise sufficiently fast at high temperatures, a third term can be added, making it—

$$Q=\alpha t+\beta t^2+\gamma t^3$$

It has been found that formulæ of this kind will fit within the errors of experiment almost all the observations on specific heats so far made, and in most cases the formula of two terms answers perfectly. The third term seems to be needed only when the curve is approaching the melting point or a critical point of the substance, when part of the heat necessary for a change of state seems to be absorbed before the point itself is actually reached. At temperatures distant from these points only two terms are needed in the formula.

Suppose, now, that a series of experiments have been made with a metal, and it is wished from the data obtained to construct the formula reckoned to zero. For a body cooling from $t_2$ or $t_1$ to zero the formula gives—

$$Q_1=\alpha t_1+\beta t_1^2$$
$$Q_2=\alpha t_2+\theta t_2^2$$

therefore, for a body cooling from $t_1$ to $t_2$, the amount of heat given out must be—

$$(Q_1-Q_2)=\alpha(t_1-t_2)+\beta(t_1^2-t_2^2) \qquad (2)$$

Having measured the quantity of heat given out in the different experiments between various high and low temperatures, the values of $(Q_1-Q_2)$, $t_1$ and $t_2$ can be substituted in equation (2), and thus each experiment gives us some relation between $\alpha$ and $\beta$; therefore any two experiments will give us two equations from which the value of these unknown coefficients may be derived. Two other experiments might give slightly different values for $\alpha$ and $\beta$, and thus several slightly varying values could be obtained and their average taken as the true values. A much neater and more accurate way, however, is to substitute the data obtained in each experiment in equation (2), thus obtaining as many equations of condition as there are experiments made, and from these calculating the most probable values of $\alpha$ and $\beta$ by the method of least squares. The formula thus derived will give a curve which will pass through the mean of all the observations made.

If we divide the heat given out by a substance falling from $t$ to zero by the range of temperature $t$, we get the mean value of the specific heat between those temperatures; therefore—

$$S_m=\frac{Q}{t}=\frac{\alpha t+\beta t^2}{t}=\alpha+\beta t. \qquad (3)$$

Or, if the substance does not fall to zero, but from $t_1$ to $t_2$,—

$$S_m=\frac{Q_1-Q_2}{t_1-t_2}=\frac{\alpha(t-t_2)+\beta(t_1^2-t_2^2}{t_1-t_2}. \qquad (4)$$
$$=\alpha+\beta(t_1+t_2).$$

If we evaluate equation (2) for two temperatures within 1° of each other, we obtain the heat given out for a fall of 1°; that is, the actual or true specific heat at that temperature. A much more elegant method, however, is to take the first differential coefficient of the equation representing the heat given out in falling to zero [equation (1)], and we thus obtain the equation for the *ratio* of the heat given out to the fall in temperature which is the true specific heat.

Therefore, taking—

$$Q=\alpha t+\beta t^2+\gamma t^3,$$

we have—

$$S=\frac{dQ}{dt}=\alpha+2\beta t+3\gamma t^2.$$

Or, leaving out the third term as before,—

$$S=\alpha+2\beta t. \qquad (5)$$

This formula is very similar to equation (3) for the mean specific heat, both of them being the formulæ of straight lines, starting when $t=0°$ at the value $\alpha$, which is therefore the true specific heat of the body at zero. The formula for the true specific heat can thus be easily deduced from that for the amount of heat; and it is this quantity which has an intimate dependence on the properties of the substance at any given temperature. For this reason the diagrams which follow show the variations of the *true* specific heat with the temperature.

(There were here thrown upon the screen a number of diagrams, with running comments by the lecturer. It has been thought advisable in printing the lecture to incorporate these diagrams into an Appendix, in which is discussed the specific heat of each of the metals separately at a length which would have been impossible, and indeed undesirable, during the delivery of the lecture.)

## V.

The heat or energy absorbed by a substance for 1° rise of temperature is divided up in the body into several parts. One fraction of it does external work, if the substance is free to expand. The amount of this for solids and liquids is so small as to be negligible, but for gases it amounts to as much as two-fifths of the whole specific heat. As far as the metals are concerned, we can neglect it. A second fraction of the energy absorbed goes to increasing the energy of atomic motion within the molecule. For solids and liquids, where the molecule is complex, this will amount to a considerable portion of the whole; for gases it is a much smaller fraction. The third and last part of the energy absorbed may be considered as going to increase the energy of vibration of the molecules as a whole—that is, increasing the temperature of the substance; for, on the mechanical theory of heat, the temperature of a body is measured by the energy of vibration of its molecules as a whole. We can therefore put—

$$Q=\text{molecular energy}+\text{atomic energy}+\text{external work}.$$

Leaving out of the discussion the last term, we may say that the proportion which the first two terms bear to each other or to the whole has not been solved for solid and liquid bodies, but has been worked out very satisfactorily for gases, especially by Clausius and Naumann.

The most striking law which has been discovered regarding specific heats is the law of Dulong and Petit, which affirms that they vary inversely as the atomic weights of the elements. The metals behave very well in this respect, the products of their atomic weights and specific heats being all nearly the same. But, in order to attain this uniformity, the metals must be compared at ordinary temperatures, since the specific heats vary so greatly. Iron, for instance, gives the usual product, about 6·3, if the specific heat at 50° is taken; but if its specific heat at 900° were taken this product would be just about double. But the fact remains that there are slight variations in the products (atomic heats) at ordinary temperatures, and much speculation has been indulged in regarding their causes. In some instances a great variation has been due to incorrect determinations of the specific heat, or from the specimen used not being perfectly pure. Manganese, for instance, has never been obtained perfectly free from silicon or carbon, either of which increases its specific heat; while aluminum has generally been used containing iron, which decreases its specific heat. Determinations with the chemically pure metal would give in both cases atomic heats nearer the average. Yet, allowing for this source of error, there are still variations to be explained, and the only reasons we can assign are that the metals are in different states of aggregation, requiring different amounts of work to overcome the interior cohesion of the particles or to elongate the metal. It is possible, therefore, that the differing densities, hardness, and strength of the metals are the various disturbing influences which prevent their atomic heats from being exactly alike at ordinary temperatures.

Some investigators have tried to bring these facts into the calculation and take strict account of them. P. Joubin, for instance, states that for any metal the product of the specific heat and specific gravity (which would be the specific heat of unit volume) is proportional to the product of the modulus of elasticity into the [linear ?] coefficient of expansion by heat. H. Fritz states that the product of the atomic heat, the specific heat of unit volume, and the cube root of the atomic volume, is equal to the cube root of the absolute temperature of the melting-point into the specific heat of unit volume divided by 1·28; that is,—

$$(\text{At. ht.}) \times (\text{sp. ht. unit vol.}) \times (\text{at. vol.})^{\frac{1}{3}} = \text{M.P.}\left(\frac{\text{sp. ht. unit vol.}}{1{\cdot}28}\right)^{\frac{1}{3}}$$

Fritz claims to have verified this formula for forty-eight of the elements; but I cannot offer any remarks, not having seen the original paper.

Weibe holds that the amount of heat necessary to raise an element from the absolute zero to its melting-point (taking atomic weights) is inversely apportioned to its coefficient of cubical expansion. This rule holds good for some of the elements, especially for those crystallising in the isometric system, but there are many exceptions to it, so that it is not a satisfactory solution of the problem of reconciling the differences in the atomic heats.

A rule of somewhat similar nature has been discovered by the writer, applying to the latent heats of fusion. I have found that the latent heat of fusion of the metals is frequently a simple fraction of the heat required to raise the metal from the absolute zero to its melting-point. It is in many cases simply one-third. Let us illustrate by several examples, referring to the previous discussions for the data:—

| | Calories. |
|---|---|
| *Tin.*— | |
| Bede's formulæ would give for the heat from absolute zero to melting-point | 27·6 |
| One-half of this would be | 13·8 |
| Observed by Person | 13·73 |
| Observed by Richards | 14·56 |
| *Silver.*— | |
| Pionchon gives from M. P. to 0° | 60·32 |
| Formula suggested gives (0° to 273°) | 14·45 |
| Total heat to absolute zero | 74·77 |
| One-third of this | 24·92 |
| Observed by Pionchon | 24·72 |
| *Platinum.*— | |
| Gives in cooling to 0° (Violle) | 75·21 |
| From 0° to −273° (Violle's formula) | 8·19 |
| Total to absolute zero | 83·40 |
| One-third of this | 27·80 |
| Observed by Pionchon | 27·18 |
| *Cadmium.*— | |
| Naccari's formula gives the mean specific heat to absolute zero 0·05, from which the total heat would be | 29·70 |
| One-half of this | 14·85 |
| Obtained by Person | 13·66 |
| *Zinc.*— | |
| Le Verrier gives as the heat to 0° | 46·9 |
| Formula (Bède's) gives from 0° to 273° | 24·3 |
| Total heat to absolute zero | 71·2 |
| One-third of this is | 23·7 |
| Obtained by Person (corrected) | 22·6 |

*Bismuth.*—

Taking Bède's formula, and correcting it so that it passes through Regnault's value, we get the equation—

$$Q = 0{\cdot}0308\,t + 0{\cdot}00002\,t^2,$$

| | |
|---|---|
| which gives for −273 to +266·8 | 16·57 |
| One-half of this would be | 8·28 |
| Obtained by Person (corrected) | 8·88 |
| *Copper.*— | |
| The formula worked out by the writer gives from −273° to 1054 | 143·0 |
| One-third of this is | 47·7 |
| Observed | 43·3 |
| *Palladium.*— | |
| Gives out to 0° (Violle) | 109·8 |
| From −273° to 0° (Violle's formula) | 15·1 |
| Total to absolute zero | 124·9 |
| One-third of this is | 41·6 |
| Obtained by Violle | 36·3 |

(Violle remarks that this was an experiment of unusual difficulty, and that the result is approximate.)

| | |
|---|---|
| *Mercury.*— | |
| Taking Regnault's value for the specific heat of solid mercury, we have for the total heat from absolute zero to −40° | 7·46 |
| One-third of this | 2·49 |
| Obtained by Person | 2·84 |
| *Alloys.*— | |
| The rule applies probably to alloys also; for instance, d'Arcet's Fusible Alloy. Its specific heat at 30° is 0·062 (Spring). The mean between 96° and −273° is very probably smaller than this, but how much we cannot say, probably 10 per cent. However, the above value would give for the heat from absolute zero | 22·88 |
| One-third of this is | 7·63 |
| Observed by Person | 5·96 |

With metals having a small latent heat of fusion the inaccuracies of the formulæ for the specific heat may introduce relatively large errors. After all, there are too many deviations and variations to enable us to claim any strict rule regarding these coincidences. All that I wish to do is to call attention to the fact that for bismuth, cadmium, and tin, the latent heat of fusion is very nearly one-half the total heat in the solid metal at its melting-point, while for silver, platinum, zinc, copper, palladium, mercury, and d'Arcet's alloy it is close to one-third. The latent heat of fusion of silver may be assumed as probably the most accurate known, as also the curve of its specific heat, and in this very case the proximity of the ratio to one-third is the closest.

I might close by venturing a prediction. The best results we have for *gold* would indicate about forty-two calories as the amount of heat contained in the solid metal at the melting-point. If the ratio in this case is one-third, as its similarity to silver, copper, and platinum might indicate, its latent heat of fusion would be about fourteen calories. It has not yet been determined, to my knowledge.

(To be continued.)

## NOTICES OF BOOKS.

*The Law of Cremation.* An Outline of the Laws relating to Cremation, Ancient and Modern; together with the Rules and Regulations of various Cremation Societies at Home and Abroad. By Aubrey Richardson, Solicitor. London: Reeves and Turner. 1893.

In this age of great cities the disposal of the dead must continually become a more pressing question. The work before us is, therefore, calculated to be very widely useful. It lays before us the essential features of the cremation controversy, showing the benefits to be derived by the use of fire in place of interment, and it shows the one sole difficulty to be avoided. This difficulty, it need scarcely be said, relates to the detection of poisons. At present if after death and burial suspicion should arise that some person has not come by his death fairly, the body can be exhumed and submitted to chemical and microscopical examination. After cremation, this is in most respects out of the question. But the author very justly says that "exhumation is at best a clumsy attempt to rectify culpable want of care before burial." If a body has been in the earth for, say, three or four weeks, the chance of identifying any poison found in the remains will be very much lessened. Some of the organic poisons may have escaped or undergone decomposition. Ptomaines may have been generated in the tissues, and may greatly complicate the issue. It may be pleaded—as has actually occurred in Germany—that arsenic present in the soil of the cemetery has been absorbed by the corpse. To meet this plea it became necessary to institute analyses of the wood of the coffin and of the soil both within the grave and at different distances on either hand. Surely it would be better for every corpse to undergo a due examination by a qualified medical man, who would be authorised to hand it over to the coroner if the circumstances demand.

Hence we feel justified in asserting that the general adoption of cremation, instead of promoting, would check, secret murders.

The sanitary advantages of cremation as compared with burial are most striking, especially in cases of epidemics. Accordingly, in Brazil and La Plata during visitations of yellow fever, the cremation of the dead is obligatory.

In this country cremation is legal, though unfortunately a man cannot leave any binding directions for his remains to be destroyed by fire. In that respect we are in a worse position than are our neighbours in several European countries and in the Unites States of America.

If the opponents of cremation have not many valid arguments at their disposal, they have at any rate a catch-word which is a great thing in a country governed by catch-words. They love to talk about "Christian burial," insinuating that any other way of disposing of the dead is un-christian, or even anti-christian. If such objectors will consult the work before us, they will find that interment might rather be termed Islamite than Christian.

One of the most formidable opponents of cremation is so-called "funeral reform"; burial, not in stout coffins, but in light wicker cases. This slight modification is asserted to change the character of putrefaction. Chemists will at once repudiate this contention. But the general public may be reminded that, according to the observations of Pasteur, some oxen shot by way of stamping out the cattle plague and buried—of course, without coffins—to the depth of three yards were able to impart the disease to some sheep afterwards penned over their grave. Hence it does not seem as if decomposition could be rendered less virulent by a different mode of interment.

Mr. Richardson's work may be strongly recommended to sanitary reformers, and especially to municipal authorities. It is calculated to generate a healthier tone of thought on the cremation question.

*Ozone: its Commercial Production; its Applications.* By Emile Andreoli. London: H. Alabaster, Gatehouse, and Co.

If, as the author informs us, "no book has been published on ozone, its production and its commercial applications," it has been the subject of no little ink-shed in the form of memoirs and discussions. As regards its nature, we have about arrived at an agreement; but on its properties and its applications there is still much variety of opinion, as we find here shown in a series of paragraphs and extracts from the scientific journals and transactions extending from 1840 to the present day. Schönbein, the discoverer of ozone, seems to hold different views at different times; asserting on one occasion, in a letter to Faraday, that ozone is a compound of oxygen and hydrogen, and afterwards attacking Williamson for saying that hydrogen is one of the components of ozone!

There is mention here made of Fehling's most injudicious proposal to call ozone "electrical gas"—a step the more to be condemned as other gases may be obtained by electrical action, and as ozone itself may be produced without such action.

In speaking of the possible applications of ozone, in connection with the researches of Fröhlich, the author asks "why has not ozone been tried for disinfecting rags?" The question is here whether ozone will disinfect rags better and more cheaply than it can be done by high temperatures? It may seem hypercritical to remark that in this connection Signor Andreoli speaks of the "phylloxera microbe." Now the phylloxera is no microbe, but an insect. It is possible that ozone might kill this pest if it could be passed into the soil in sufficient quantity; but what about the working cost?

In like manner we may raise a question about the purification of sewage by means of ozone, as here suggested. To decompose the ammonia present in such waters into its constituents would be a doubtful policy. We want the ammonia as plant food.

On p. 68 we read:—"No one can state that ozone destroys *all* germs and bacteria. This is an Utopia." But we do not want all microbia destroyed; many of them are harmless, many more useful and even necessary. If we can destroy the morbific micro-organisms we shall have effected all that we need desire in this direction.

The remarks on the possible industrial applications of ozone are suggestive, and ought to draw the attention of inventors, many of whom are engaged with devising new forms of mischief, which they might well abandon in favour of the possibilities held forth in this little work.

The bibliography at the conclusion will be found very useful.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

**Note.**—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 2, July 10, 1893.

**Nomination.**—M. Bichat was elected a correspondent of the Academy for the Section of Physics.

**Pyrosulphochromic Hydrate.**—A. Recoura.—If into a solution of chromopyrosulphuric acid,—

$$(S_2O_7H)_4Cr_2(OH)_2,$$

there is poured a concentrated acid—hydrochloric, nitric, or sulphuric—there is produced a greenish white precipitate, which is the hydrate in question, $(S_2O_7)_2Cr_2(OH)_2$. This precipitate is soluble in pure water, yielding an opalescent yellowish green solution, which has the property of precipitating all metallic solutions.

**The Compounds of Selenious Acid with the Molybdates, and on Molybdoselenious Acid.**—E. Péchard.—The author has formerly shown that sulphurous acid may combine with the alkaline molybdates to form molybdosulphites. Selenious acid forms analogous compounds which are more stable. The author has described the ammonium, potassium, sodium, and barium salts. Molybdoselenious acid is obtained by decomposing the barium salt with the equivalent quantity of sulphuric acid. The clear yellowish filtrate forms, on concentration, a syrupy mass which does not crystallise.

**Arsenic and Antimony Iodosulphides.**—L. Ouvrard.—The author has obtained the compounds $As_2S_5I$, $AsSI_2$, and $AsS_2I$. With antimony the author obtained $SbS_2I$, a vermilion-red compound formed of entangled leaflets. Another compound, $SbS_2I_3$ is soluble in dry carbon disulphide, and readily decomposed with moist air.

**The Dissociation of Calcium Plumbate.**—H. Le Chatelier.—Some time ago Kassner proposed to use this compound in place of barium peroxide for obtaining oxygen. If heated, it gives off a part of its oxygen; the reaction being $PbO_2,2CaO = PbO + 2CaO + O$. The dissociation takes place at a higher temperature than that of barium peroxide. The heat for the latter substance is 700°, whilst that for calcium plumbate is 900. This is a great inconvenience, on account of the increased consumption of fuel and the more rapid corrosion of the iron retorts. On the other hand, the plumbate has a great advantage over baryta, by absorbing oxygen more rapidly and more completely, and it does not require the air to be previously dried and freed from carbonic acid.

**On Benzoylcinchonine.**—E. Léger.—This compound, which was first obtained by Schützenberger, is found in prismatic crystals, inodorous and colourless. It is insoluble in water, but very soluble in alcohol and in ether saturated with water. It constitutes the true benzoic ether of cinchonine considered as a phenol. It acts upon polarised light, and is slightly lævorotatory.

**Action of Sulphuric Acid upon Pyrocatechin and on Homopyrocatechin.**—H. Cousin.—The barium salt of pyrocatechin has the formula—

$$[C_6H_3(OH)_2SO_3]2Ba + 4H_2O.$$

That of homopyrocatechin is—

$$[C_7H_5(OH)_2SO_3]2Ba + 3H_2O.$$

**Process for the Direct Combination of Ethylenic and Aromatic Carbides.**—A. Brochet.—Several syntheses have been of late effected by the direct union of the methyl groups of the methylbenzenes with cinnamene in presence of sulphuric acid. The author generalises this action, and thinks that the carbides of the ethylenic series must combine with benzene and its derivatives. With amylenes the yields are less good than with normal hexylene. Toluene behaves in the same manner as benzene.

**Attempt at the Diagnosis of the Isomeric Amidobenzoic Acids, and of some other Aromatic Compounds.**—Oechsner de Coninck.—We may distinguish the amidobenzoic and nitrobenzoic isomers and the diphenols by preparing their alcoholic or ethereal solutions and exposing them to the solar rays or to diffused light. The diagnosis is possible, not only by the different colourations which appear, but by the greater or less stability of the tints produced on exposure to light, and the very different times in which they appear.

**On Geraniol.**—Ph. Barlier.—The linalol of the essence of spike lavender is nothing less than the instable stereoisomeric modification of geraniol, playing with it the same part as does licareol with licarhodol.

**Influence of the Acidity of Worts on the Composition of the Phlegms.**—L. Lindot.—The phlegms obtained from acidulous worts contain more higher alcohols than those from worts not acidulated, but they contain less bases, volatile acids, and ether, and must hence be regarded as of a better quality.

**The Greater Assimilability of the Nitric Nitrogen of Nitrates recently formed.**—P. Pichard.—The preference accorded to sodium nitrate as compared with potassium nitrate as a chemical manure is justified, not merely by its price, but by a greater efficacy resulting from its transformation into sulphate in a soil well supplied with potash. The practice of spreading soda and saltpetre in small repeated doses serves not merely to avoid loss from its being washed away, but to furnish the plants with potassium nitrate of recent formation.

**Honeydew of the Lime Tree.**—M. Maquenne.—This exudation is similar to the manna of the larch studied by Berthelot, and to that of *Alhagi camelorum*. Its presence is due to a parasite.

Vol. cxvii., No. 3, July 17, 1893.

**On the Simplicity of Samarium.**—Eug. Demarçay.—Lecoq de Boisbaudran has recently entrusted to me four solutions obtained from a fractionation of samarium, in order that I should examine their spectrum of absorption in the violet region. These fractions comprise:—1. The tailings of the fractionation by ammonia. 2. The middle portion of this fractionation. 3. The head of the fractionation by oxalic acid from the head of the fractionation by ammonia. 4. The tailings of the same fractionation by oxalic acid. I may summarise these observations very simply by saying that these four portions gave essentially the spectrum of samarium with a trace of neodymium in No. 1, and a trace of the earths of erbia (?) in No. 3 and especially No. 4. The spectrum of samarium did not present the slightest variation in these four portions. This led me to re-examine the products in which I thought I had detected signs of the variation of the spectrum of samarium, and which led me to assume the presence of two distinct substances in this element. This view has since been put forward anew by several chemists. According to this new examination, it does not seem to me justified. These variations have, in fact, been observed in solutions rich in didymium. If we examine the spectrum of a rather concentrated nitric solution of neodymium, we observe along with the strong ray ($\lambda = 427.5$) a weak band, very vague, and spread out ($\lambda = 418$) about, which almost coincides with one of the strong bands of samarium even in the absence of all the bands of this element. On contracting the slit of the spectroscope, this band always remained simple and vague. On the other hand, if we examine the acid nitrate of samarium with the same narrow slit we perceive that the band of Lecoq, Soret, &c., is composed of two relatively narrow rays ($\lambda$ 415 and 419). The middle of the band of the salts of neodymium coincides almost with the more refrangible margin of the less refrangible ray. It is thus easily understood that with a broad slit and solutions rich in didymium this double band has a variable aspect. I have also observed in the spectrum of the four portions—though in a manner too uncertain to know if their intensity varied—three small bands rather more refrangible than H. Pure neodymium does not show these rays. I conclude that hitherto there is no room to suspect the simplicity of samarium on grounds drawn from the variability of the absorption-spectrum of these solutions.

**On the Cyclic Condensations of Carbon.**—Gustave Rousseau.—This paper will be inserted in full.

**On Aminobutenediamide and Butanonediamide.**—R. Thomas Mamert.—To the former of these bodies the author assigns the formula—

$$CONH_2.C(NH_2)=CH.CONH_2.$$

He has examined its behaviour with potassa and with copper sulphate. Butanonediamide forms white crystals which melt and are decomposed at 180°. It is moderately soluble in water, and the solution gives with ferric chloride a characteristic ruby-red colour.

**Rotatory Powers of the Derivatives of Quineic Acid.**—S. G. Cerkez.—This paper consists chiefly of tables. It appears that the introduction of hydrocarbon radicles and metals diminishes the rotatory power of quineic acid. The other organic bases, except diethylamine, do not combine with quineic acid in an alcoholic solution.

**Derivatives and Constitution of the Rhodinol of the Essence of Roses.**—Ph. Barbier.—If rhodinol is submitted in a closed vessel to the action of acetic anhydride at 180° there is merely formed rhodinolacetic ether, $C_{10}H_{17}OC_2H_3O$, a colourless mobile liquid of an agreeable odour, boiling at 131° under a pressure of 15 m.m. Its specific gravity at 0° is 0·9214. If saponified by alcoholic potassa this ether is re-converted to rhodinol without any change of properties.

### *Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxiii., No. 1.

**Volumetric Determination of Iron by Stannous Chloride.**—L. L. de Koninck.—The objection to the volumetric determination of iron by means of stannous chloride has been the difficulty of detecting the end of the reaction. The remedy generally employed has been the addition to the solution of a little cobalt chloride. The green tint thus produced passes to a decided blue as soon as the last trace of the ferric chloride is reduced. R. W. Mahon proposes another indicator composed of a solution of mercuric chloride containing 34 grms. of this salt per litre. There is further added a trace of platinic chloride containing 0·05 grm. of platinum. For a determination he employs 15 c.c. of this solution.

## MISCELLANEOUS.

**Thermometers for Low Temperatures.**—The International Meteorological Commission having intimated its desire that the International Bureau of Weights and Measures should supply the National Meteorological Institutes with first-class standard thermometers descending to about −70°, these instruments were put under study in 1889. After many experiments the results proved very satisfactory. M. P. Chappuis, of the International Bureau, gave a report of these experiments at a recent meeting of the Swiss Society of Natural Sciences. In the first place, the thermometric liquid had to be chosen. Alcohol, hitherto employed almost exclusively, has great inconveniences; from the outset, therefore, toluene was studied, together with alcohol. Toluene is of greater fluidity, and has a much higher boiling-point (111° about), which enables determination of the average degree, by employing the graduation of the mercury thermometer, 0° and 100°. Some thermometers, with a tube of about 0 6 m.m. in diameter, were filled with mercury and carefully measured, then emptied and filled with alcohol or toluene; they were then compared with the hydrogen thermometer in a bath of alcohol, which was cooled by the expansion of carbonic acid in the annular space. The flow of gas, passing by a tube, was regulated by means of a point-cock with regulator; thus the temperature was kept very constant in the interval of −40° to −75°; between 0° and 40° chloride of methyl was employed instead of carbonic acid. Before these comparisons, care was taken to fix the points 0° and 100° very exactly in the toluene thermometers, and 0° and 30° for the alcohol thermometers; for these two kinds of thermometers the indications were referred to the average degree of these two respective intervals. The thermometers were made in such a way that at the highest temperature of graduation the space below the liquid was sufficient for the pressure to remain within rather low limits. Comparisons of many instruments, carefully examined, showed that thermometers filled with toluene, pure and well dried, agree with each other to nearly $\frac{3}{100}$ of a degree, as far as −70°. Various samples of alcohol, considered pure, gave very great differences; for example, between alcohol purified in the laboratory of the Eçole Normale, under the management of M. Joly, and a sample of pure alcohol from the firm of Billault, a difference of 1° was found at −70°. The following Table gives the readings of toluene and alcohol thermometers for different temperatures of the hydrogen thermometer:—

| Hydrogen. | Toluene. Graduated from 0° to 100°. | Pure alcohol. Graduated from 0° to 30°. |
|---|---|---|
| +100 | 100 | 30 |
| +50 | 26·9 | 0 |
| 0 | 0 | 0 |
| −10 | −8·54 | −9·31 |
| −20 | −16·90 | −18·45 |
| −30 | −25·10 | −27·44 |
| −40 | −33·15 | −36·30 |
| −50 | −41·08 | −45·05 |
| −60 | −48·90 | −53·71 |
| −70 | −56·63 | −62·31 |

We find that the toluene, like alcohol, contracts less and less as the temperature falls. The above table might lead one to suppose that there is less difference between the alcohol and hydrogen thermometers than in the case of toluene; this difference is due simply to the fact that the points selected for its graduation are much nearer. Other liquids are being tried, but as yet toluene seems the best. Considering the increasing importance of researches at low temperatures, physicists will be glad to be able to attain, easily, an accurateness of $\frac{1}{20}$ of a degree.—*La Nature.*

THE CHEMICAL NEWS.

VOL. LXVII., No. 1760.

## THE CHEMICAL HISTORY OF THE ATMOSPHERE.

By Dr. T. L. PHIPSON, F.C.S., &c.

I DESIRE to lay before my readers, in a set of brief propositions, the chemical history of the atmosphere from its origin to our own day, as the result of observation and experiment, including the consequences of the theory deduced from the observations I have already published in the CHEMICAL NEWS during March, June, and July, 1893.

I. In the origin the matter of the Earth was in a gaseous or nebulous state, but a gas placed in such conditions of heat that no compounds could exist. Our world was then all atmosphere, if I may be allowed to use such an expression; but a superheated gas in which the atoms were all free, and *identical in nature*.* The first result of loss of heat was the formation of atomic systems, similar to those systems which are recognised by astronomy; in other words, the formation of *elements* (groups of atoms) which combined according to the laws of affinity.

In time a solid crust covering the internal molten mass was thus formed, water was condensed upon the irregular volcanic surface, and an atmosphere surrounded the globe.

II. The primitive atmosphere was composed of nitrogen, the substance which has the least tendency to combine directly with others. Into this atmosphere volcanic action evolved large quantities of carbonic acid and water, as is still the case, on a smaller scale, at the present time.

There was no free oxygen in this primitive atmosphere, because we find combustible substances in the primitive rocks (sulphides, graphite, protoxides, &c.). It was in this primitive atmosphere of nitrogen, with more or less carbonic acid and vapour, that the first organised beings (plants) made their appearance. My experiments have shown that many plants of our own day can vegetate in an atmosphere of this kind, in which animal life is quite impossible.

III. Plants even of the lowest orders, such as the *Protococcus*, in vegetating evolve oxygen copiously, apparently more copiously (weight for weight) than the higher plants; and this oxygen, derived by plants from the carbonic acid supplied by volcanic action and abundantly diffused in the earth and its primitive atmosphere, has been poured into the air for an incalculable series of ages, through periods of such vast duration that the mind of man can form no conception of them, until it has acquired the chemical composition we find at the present time.

IV. The oxygen of the atmosphere has thus gone on increasing in quantity from the earliest ages of the Earth's history until the present time; and when it had attained to a certain amount, animal life became possible, and duly appeared. At the same time carbonic acid has diminished, since the strata of the Earth reveal immense deposits of carbon (coal, lignite, peat, &c.) which was originally present in the air as carbonic acid.

V. When the oxygen thus derived from plant-life was present in the air in much smaller proportions than we now find it, the lowest animals in the scale, whose respiratory functions required less oxygen, could exist.

As the oxygen became more abundant animal life of a higher order became possible, and we find that the development of the nervous system—the highest characteristic of animal life—has coincided with the increase of oxygen in the air.

VI. It is possible that the increase of oxygen and diminution of carbonic acid still continues at the present time, but so slowly that it is perhaps impossible to put the change in evidence by chemical analyses, even supposing the latter to be made at intervals of more than a century. Nevertheless the latest and most careful determinations of carbonic acid in the air have shown a decided decrease in the last fifty years (0·05 to 0·03).

Putney, August, 1893.

## THE FORMATION OF HYDROCYANIC ACID BY THE ACTION OF NITRIC ACID UPON SUGAR, &c.

By F. B. BURLS, R. E. EVANS, and C. H. DESCH.

IN the course of a preparation of oxalic acid from cane-sugar, by the usual method of oxidation by nitric acid, one of the writers (F. B. B.) noticed the formation of hydrocyanic acid, a fact which we believe has not been previously remarked. The experiments which we shall describe show that this compound is formed in perceptible quantities during the reaction.

The proportions employed in the preparation were 3 parts of crystallised cane-sugar, 2 parts nitric acid, and 1 part water. Hydrocyanic acid was first detected by its smell, just after the first violence of the reaction had subsided and the evolution of nitrous fumes had slackened. The flask containing the mixture was therefore attached to a condenser, and the products distilled. The distillate smelt distinctly of prussic acid, whose presence wss confirmed by the usual test.

In subsequent repetitions of this experiment it was found that when the formation of HCN ceased, owing to the nitric acid being exhausted (which is readily seen by the darkening of the solution in the distilling flask), the addition of more acid caused the evolution to recommence, and in this way a considerable quantity of HCN could be obtained. The process was also tried continuously, the nitric acid being allowed to drop slowly into the sugar solution from a tap-funnel, this method giving very good results.

The sugar was also replaced by caramel, the formation of HCN being again evident, though the quantity produced was smaller than before.

This being the case, it was thought advisable to ascertain whether carbon itself, when acted upon by dilute $HNO_3$, gave hydrocyanic acid among the products. Finely-divided charcoal was therefore heated with dilute nitric acid (1 to 4) in a closed bottle in the water-bath for some hours. On releasing the pressure a large quantity of carbon dioxide escaped. The liquid on distillation showed the presence of HCN.

We may here mention that the prussian blue test does not answer when a little $HNO_3$ distils over with the HCN.

The same result was obtained when cane-sugar was acted upon by nitrous acid, being first digested with $KNO_2$, sulphuric acid being then added and the liquid distilled.

It thus appears that hydrocyanic acid is a normal product of the reducing action of carbon and certain carbon compounds upon nitric or nitrous acids. The exact course of the reaction is perhaps not very obvious, though in the case of carbon it may readily be expressed by an equation—

$$2HNO_3 + C = 2HNO_2 + CO_2$$
$$HNO_2 + 2C = HCN + CO_2.$$

According to this the HCN is really produced by the action of the nitrous acid.

Analytical Laboratory, Stratford-on-Avon.

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* Phipson, "Outlines of a New Atomic Theory." London, 1886.

# STUDY OF CERTAIN NOVEL PHENOMENA OF FUSION AND VOLATILISATION PRODUCED BY MEANS OF THE HEAT OF THE ELECTRIC ARC.*

By HENRI MOISSAN.

In the investigation which we now present, we insist especially upon the volatilisation of metals and metallic oxides.

When it is required to condense the vapours of bodies which are volatilisable with difficulty at high temperatures we use a metal tube cooled internally by a current of water. We employed a U-tube of copper of 15 m.m. in diameter, traversed by a current of water having a pressure of about 10 atmospheres. The curved part of the U-tube was introduced into the electric furnace at 2 c.m. from the arc above the crucible which contained the substance to be volatilised. Further, a sheet of asbestos pasteboard placed at the aperture which gave passage to the cold tube rendered it possible to condense the metallic vapours which issued from the furnace in abundance.

As an instance of the use of the cold tube, we cite the action of heat upon two stable mineral compounds, magnesium pyrophosphate and silicate.

Magnesium pyrophosphate was exposed for five minutes in the electric furnace to the action of an arc of 300 ampères and 65 volts. After a few moments there was aa abundant escape of vapours. The cold tube placed in the apparatus at the outset was traversed before the experiment by a current of water at 15·4°. At the end of the experiment, whilst the furnace was still in full activity, the temperature of the water was only 17·5°. The vapours produced in the furnace were condensed with the greatest ease on the cold tube. When it was withdrawn from the furnace it was found covered in part with ordinary phosphorus, which took fire on friction and became slowly oxidised in the air, yielding a syrupy deposit which readily reduced silver nitrate. Besides this phosphorus we found evidence of the presence of magnesia on the tube.

In another experiment we heated asbestos (magnesium silicate containing a little iron) in a coke crucible for six minutes. The current measured 300 ampères and 75 volts. After the experiment there remained in the crucible merely a very small quantity of melted silicate and a ferruginous globule with a brilliant fracture, containing 1·6 of magnesium and 0·7 of silicon.

The cold tube was covered with a grey powder, containing a large excess of silica, magnesia, and very small quantities of carbon and silicon. We found in it spherules of transparent silica, which scratched glass, and gave distinctly the reaction of silica with a bead of phosphorus salt.

These two preliminary experiments, selected from among many others, demonstrate that the most stable salts are dissociated at the temperature of the arc, and that it is possible to collect the products of their decomposition and to study them with convenience.

### *Volatilisation of Metals.*

*Copper.*—A fragment of copper of 103 grms. is placed in the coke crucible of the electric furnace. It is heated for five minutes with a current of 350 ampères and 70 volts. After a minute or two brilliant flames of 0·04 to 0·05 metre in length issue forcibly by the apertures which give passage to the electrodes on each side of the furnace. These flames were surmounted by clouds of a yellow smoke due to the formation of copper oxide from the combustion of the metallic vapour.

After five minutes the current was stopped, and the regulus remaining in the crucible weighed only 77 grms. Hence 26 grms. of copper had been volatilised.

All around the crucible, in the horizontal part between the furnace and the cover, there was found a large halo of globules of melted copper, coming from the distillation of the metal. The yellow vapour collected gave copper oxide to cold dilute hydrochloric acid, and left as a residue small spheres of metallic copper, blackened on their surface and soluble in nitric acid.

Abundance of metallic copper was found upon the cold tube.

*Silver.*—It has long been known that silver is volatile at a high temperature. In the electric furnace silver may be brought to full ebullition. It distils then more readily than silica or zirconia. Melted globules, an amorphous grey dust, and absorbent fragments may be collected in abundance.

*Platinum.*—If heated in the electric furnace, platinum melts in a few instants and is quickly volatilised. Metallic platinum may be collected in small brilliant globules and in dust on the cooler parts of the electrodes.

*Aluminium.*—Heated for six minutes in a current of 250 ampères and 70 volts there is obtained on the cold tube a grey powder, slightly agglomerated, which on agitation in water allows small spherules of aluminium to settle to the bottom of the beaker. These spherules have a metallic aspect; they are attacked by hydrochloric and sulphuric acids, with an escape of hydrogen. In the vapours issuing from the furnace small spheres covered with aluminium may also be collected upon asbestos pasteboard.

*Tin.*—Duration of the experiment, eight minutes; intensity of the current, 380 ampères and 80 volts. When the furnace is in full activity copious white fumes escape near the electrodes. There is found on the tube a small quantity of tin oxide, soluble in dilute hydrochloric acid, small brilliant globules, and grey substance of a fibrous aspect forming a decided felt. The fibrous portion and the metallic spheres yield with hydrochloric acid a very distinct development of hydrogen. They consist of metallic tin. It is also easy to collect on the outer part of the furnace small globules of metallic tin mixed with oxide.

*Gold.*—Duration of experiment, six minutes; current, 360 ampères, 70 volts. In the crucible were placed 100 grms. of gold; after the experiment there remained only 95 grms. During the experiment there escaped abundant fumes of a greenish yellow colour. The cold tube was covered with a powder of a deep colour with purple reflections. Under the microscope, with a low power, there were distinctly recognised small regular spheres of melted gold of a fine yellow colour. These spherules dissolved rapidly in aqua regia, and showed all the characters of salts of gold.

On the asbestos pasteboard, upon which the vapours of the furnace had been condensed, we recognised at the point which had been most heated numerous very minute globules of metallic gold. Around this part, which has a very distinct yellow colour, there is found a red halo and beyond that a fine dark purple.

*Manganese.*—This metal, to the volatilisation of which M. Jordan has recently called attention, has yielded very interesting results. We here describe merely a single experiment, which seems quite characteristic. Duration of heating, ten minutes; current, 380 ampères and 80 volts. There were placed in the crucible 400 grms. manganese. Very abundant fumes escaped, and at last there remained merely an ingot of metallic carbide weighing a few grms.

If in the preparation of manganese in the electric furnace the heat is too much prolonged, no metal is found in the crucible.

*Iron.*—Duration of heating, seven minutes; current, 350 ampères, 70 volts. There was collected on the cold tube a grey powder presenting some brilliant surfaces, very slender and warty, malleable enough to double up under the blade of a knife, mixed with a grey dust having the appearance of iron reduced by hydrogen. This dust

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* From the *Comptes Rendus*.

becomes brilliant under the burnishing-steel, and the entire specimen dissolves in dilute hydrochloric acid with an escape of hydrogen. Upon the asbestos pasteboard upon which the metallic vapours are condensed there are collected small globes of magnetic oxide, and globules of the same compound of a black colour and a wrinkled surface.

*Uranium.*—Duration of the experiment, nine minutes; current, 350 ampères, 75 volts. We can collect upon the cold tube small metallic spheres, solid and abundant, mixed with a grey powder easily soluble in acids, with an escape of hydrogen. The solution presents all the characters of salts of uranium. Upon the asbestos pasteboard we find abundant yellow spheres which, if crushed in an agate mortar, lose a crust of oxide, become grey, and take a metallic aspect.

These spherules of distilled uranium contain no carbon and are not attracted by the magnet.

(To be continued.)

## ON THE DETERMINATION OF VANADIC ACID.*

THE original method of Berzelius, modified by A. Ditte, will be found in *Comptes Rendus* (civ., p. 982). The determination of vanadic acid in presence of alkaline and ammoniacal salts has been studied by A. Carnot (*Ibid.*, civ., pp. 1803 and 1850).

O. Manasse (*Liebig's Annalen*, 240, 23) uses the following methods for the analysis of the alkaline earths:—The barium salts are fused with 3 to 4 parts of sodium carbonate or sodium-potassium carbonate; the melt is treated with hot water, and the undissolved barium carbonate is filtered off. The latter was always impure, and contained as a mean 1·5 per cent of vanadic acid, which could not be completely removed even by a repeated fusion. The impure barium carbonate is therefore dissolved in hydrochloric acid, and the baryta re-precipitated as sulphate by sulphuric acid; the sulphate on examination was found free from vanadic acid.

A series of determinations was also effected by opening up with acid potassium sulphate. The substance was melted with from 5 to 6 parts of potassium disulphate, allowed to remain for a considerable time over a small flame, and the melt when cold was rinsed out of the crucible with water and a little sulphuric acid. The barium sulphate thus obtained passed very readily through the filter, but was in many cases fairly pure, as the vanadic acid present was often only 0·3 to 0·5 per cent. If, after the ignition of the barium sulphate, the presence of vanadic acid is detected on moistening with acid, the barium sulphate is dissolved in concentrated sulphuric acid, and the solution is poured into water. By means of this treatment the barium precipitate is certainly obtained perfectly free from vanadic acid; but the operation requires a long time, as the barium sulphate does not subside perfectly until after the lapse of from one to two days.

The strontium vanadates, sparingly soluble in water, are likewise decomposed by fusion with an alkaline carbonate. As the strontium carbonate thus obtained still contains vanadic acid, it is dissolved in hydrochloric acid, the solution supersaturated with ammonia, and precipitated with ammonium or potassium carbonate. The strontium carbonate thus obtained is free from vanadic acid. The separation of strontium as sulphate is less to be recommended since, in consequence of the requisite addition of alcohol, the filtrate cannot serve for the volumetric determination of the vanadic acid with permanganate.

Boiling the pulverised salts with a concentrated solution of potassium carbonate in excess gives also good results. The strontium carbonate is then further treated as above directed.

For the determination of the vanadic acid the filtrates from the strontium carbonate are mixed, supersaturated with sulphuric acid, reduced, and titrated with permanganate.

The double salts readily soluble in warm water, such as the strontium potassium vanadates, are simply dissolved by being covered with hot water, and the vanadic acid is precipitated with lead acetate. The lead vanadate is dissolved in nitric acid on the filter, the solution is evaporated with sulphuric acid until sulphuric vapours escape, diluted, the lead sulphate filtered off, and the vanadic acid determined volumetrically in the filtrate.

It is advisable to precipitate the lead vanadate from the hot solution, and to stir the liquid strongly at once. The precipitate then coagulates completely in a few minutes, whilst the supernatant liquid remains as clear as water. The lead vanadate can thus be at once easily filtered and washed with cold water. But if this precipitate is allowed to stand for some time it gradually becomes light yellow, pulverulent, and passes through the filter. After the precipitation of the lead with hydrogen sulphide, strontium and potassium are determined in the filtrate from the lead vanadate: in case of potassium sulphate traces of vanadic acid are still detected.

For the determination of vanadic acid in calcium salts the aqueous solution is simply supersaturated with sulphuric acid, and the vanadic acid is directly determined.

The latter process is applied also in the analysis of the magnesium salts. The acid magnesium vanadates are not readily soluble in cold water, but the addition of a few drops of sulphuric acid effects immediate solution.

As already intimated, the determination of vanadic acid is effected by Manasse volumetrically by means of permanganate. This method depends on the reduction of the acid solution of the vanadates to vanadium tetroxide (by means of sulphurous acid or sulphuretted hydrogen), and followed by oxidation of the tetroxide to vanadic acid by means of permanganate.

The first criticisms on this reduction were made by C. Czudnowicz (*Zeit. Anal. Chemie*, iii. 379). Subsequently H. E. Roscoe ("Researches on Vanadium," 1879) and C. Rammelsberg (*Berlin Acad. der Wissen.*, 1880) have made thorough investigations on this subject.

According to the author, when sulphurous acid was used for reduction the average result was too high, 100·18 per cent. With sulphuretted hydrogen, followed by a strong current of carbonic acid, the average result was 99·9 per cent. The author prefers the sulphurous acid method, as the colour reaction is more easily distinguished than when sulphuretted hydrogen is used, as in this case the solution always contains a little suspended sulphur.

(To be continued.)

**The Ascent of Saline Solutions in Filter-Paper.**—E. Fischer and E. Schmidmer (*Liebig's Annalen*).—Of any two salts the one which has the greater diffusion-speed ascends the more rapidly in paper; the process of diffusion can be observed in this manner as by the use of membranes. The process has the advantage of being applicable for all liquids which moisten paper.

**Attackability of Platinum and its Iridium Alloys by Sulphuric Acid.**—Heraeus (*Zeitschrift Angewandte Chemie*).—As unit he takes the loss of weight which his chemically pure platinum underwent. In an experiment made at the Gresheim works the loss on absolutely pure pure platinum was 100, that on pure platinum with 5 per cent iridium 73, on pure platinum with 10 per cent iridium 58, on a technically pure platinum made by Heraeus 90, on platinum from an English boiler 103, and on fine gold 10. Hence Heraeus now uses retorts of platinum coated with gold, which are said to be very serviceable.

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* *Zeitschrift fur Analytiscke Chemie.*

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 65).

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| MANGANESE. | | | | | | | |
| $MnSO_4Na_2SO_4+$ $+2H_2O$ | 67 | | ? | | | | |
| $MnSO_4K_2SO_4+$ $+2H_2O$ | 68 | | Tr | | | | |
| $MnSO_4HKSO_4+$ $+2H_2O$ | 69 | | Tr | | | | |
| $MnSO_4Na_2SO_4+$ $+4H_2O$ | 70 | | M | (*a*) Almond-shaped granules.<br>(*b*) Spherulitic radiating groups.<br>(*c*) Short prisms of cubic aspect. | (*a*) (*b*) Pink of 2nd order. | (*a*) *R.L.* to *e*.<br>(*b*) *R.L.* to axis of *Q.W.*<br>(*c*) Uncertain. | |
| $MnSO_4K_2SO_4+$ $+4H_2O$ | 71 | | M | In (*a*) spherulites and (*b*) confused matted masses. | Blue of 2nd order. | (*a*) $\parallel$ to axis of *Q.W.* | |
| $MnSO_4(NH_4)_2SO_4+$ $+6H_2O$ | 72 | | M | Large stumpy prisms of complex shape. | 3rd order. | — | Strong absorption with single nicol. Refraction probably near that of balsam. Small crystals cannot be seen without polarised light. |
| $MnSO_4K_2SO_4+$ $+6H_2O$ | 73 | | M | | | | |
| $Mn_2(SO_4)_3$, with sulph. of K and $NH_4$ | | *See alums.* | | | | | |
| SODIUM. | | | | | | | |
| $Na_2SO_4$ .. .. .. | 74 | Salt cake. | R | | | | |
| $Na_2SO_4+2H_2O$ .. | 75 | | R | | | | |
| $Na_2SO_4+3H_2O$ .. | 76 | | H<br>R | | | | |
| $Na_2SO_4+10H_2O$ .. | 77 | Glauber's salt. | M | Short stumpy prisms, showing many faces. | Extremely feeble: from grey of 1st order to blue of 2nd order. | Low angle to *e*. | Crystals bordered by broad dark lines. Refraction probably high. |
| $NaHSO_4$ . .. .. | 78 | | Tr† | (*a*) Long blade-like prisms.<br>(*b*) In granules or stumpy prisms with many faces. | Sometimes as high as 6th or 7th order. | Varies greatly. | Twinning not uncommon. In (*a*) the twins form penetration twins, taking the form of a cross. Outlines sharp. |
| $Na_2SO_4$ with $Al_2(SO_4)_3$ and $Cr_2(SO_4)_3$ | | *See alums.* | | | | | |

*Remarks.*

*Nos.* 70 to 73.—The salts described under these Nos. are those obtained by evaporating a mixture of $MnSO_4$ with $Na_2SO_4$, $K_2SO_4$, and $(NH_4)_2SO_4$. I know of no test applicable to microscopic specimens on glass slides for determining whether the resulting double salts contain two, four, or five molecules of water.

*No.* 72.—Some crystals have well-marked zonal lines. Others are so full of minute liquid and air bubbles as to present a dark dusty appearance under low powers. Many of the crystals show an optic axis in *c.p.l.*

*No.* 77.—Glauber's salt (mirabilite) effloresces on exposure to the air. It forms from aqueous solution between 12° and 33°. Between 33° and 40° the anhydrous salt (74) is deposited. Solubility in water is greatest at 33°, after that it declines. Between 12° a salt with seven molecules of water forms. The anhydrous salt also forms if Glauber's salt is allowed to remain exposed to the air. The anhydrous salt occurs native in thenardite and in solution in sea-water, and in some springs.

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* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

† I have followed Roscoe and Schorlemmer. Fock does not notice $NaHSO_4$, but gives $NaHSO_4+H_2O$ as a monoclinic salt.

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| SODIUM. | | | | | | | |
| $Na_2SO_4CaSO_4$ | | *See Ca.* | | | | | |
| $Na_2SO_4MgSO_4+6H_2O$ | | *See Mg.* | | | | | |
| $Na_2SO_4MnSO_4+2H_2O$ | | *See Mn.* | | | | | |
| $Na_2SO_4MnSO_4+4H_2O$ | | *See Mn.* | | | | | |
| $NaLiSO_4$ | | *See Li.* | | | | | |
| AMMONIA. | | | | | | | |
| $(NH_4)_2SO_4$ | 79 | Mascagnite. | R | Long flat prisms. Laths with rectangular tops common. | Some as high as 6th order. | *R.L.* to *e*. | |
| $(NH_4)HSO_4$ | 80 | | R | Stumpy prisms; complex shapes, six-sided outlines not uncommon. Twinning common. | Very high, probably near calcite. | *R.L.* to *e* when elongated. ‖ to twinning plane of one twin, sometimes of both. | |
| $(NH_4)_2SO_4$ with Al, Cr, &c. | — | *See Alums.* | | | | | |
| $(NH_4)LiSO_4$ | — | *See Li.* | | | | | |
| $(NH_4)_2SO_4MnSO_4+6H_2O$ | — | *See Mn.* | | | | | |
| $(NH_4)_2SO_4MgSO_4+6H_2O$ | — | *See Mg.* | | | | | |
| RUBIDIUM. | | | | | | | |
| $Rb_2SO_4$ | 81 | | R | (*a*) Six-sided plates of hexagonal habit.<br>(*b*) Lath-shaped with ragged ends.<br>(*c*) Regular well-formed crystals with complex shapes round edge of drop. | 4th order. | (*b*) *R.L.* to *e*.<br>(*c*) Various. | (*c*) Absorption with single nicol. Multiple twinning almost invariable. |
| $Rb_2SO_4Al_2(SO_4)_3+24H_2O$ | — | *See Alums.* | R | | | | |
| $Rb_2SO_4MgSO_4+6H_2O$ | — | *See Mg.* | | | | | |
| $RbLiSO_4$ | — | *See Li.* | | | | | |
| STRONTIUM. | | | | | | | |
| $SrSO_4$ | 82 | Celestine. | R | Globulites, round and almond-shaped disks, and in prisms. | White of 1st order. | In almond-shaped disks, ‖ to longer axis. | |
| $(SrBa)SO_4$ | 83 | Baryto-celestine. | R | | | | |
| TITANIUM. | | | | | | | |
| $Ti(SO_4)_2$ | 84 | Normal sulph. | — | | | | |
| $(TiO)SO_4$ | 85 | Basic sulph. | — | White hard mass. | | | |

*Remarks.*

*No.* 79.—Long rod-like liquid cavities containing air bubbles running with the length of the crystal are common. This salt is said to be isomorphous with $K_2SO_4$, but they may readily be distinguished under the microscope. There is a striking difference between them in their refraction; their double refraction is different, and the crystals of $(NH_4)_2SO_4$ are much larger and flatter than those of $K_2SO_4$. No. 79 dissolves at 0° in 71 and at 100° in 97·5 parts of water.

*No.* 80.—Very deliquescent. Aqueous solution deposits crystals, but does not completely evaporate in the open air at the ordinary temperature.

*No.* 81.—See Remarks No. 53.

*No.* 82.—Solubility in water between $CaSO_4$ and $BaSO_4$; viz., 0·015 part dissolve in 100 of water at 60° F. It is less soluble in boiling than in cold water. When $SrSO_4$ is dissolved in hot concentrated $H_2SO_4$, crystals of celestine are deposited on cooling. See Part 3.

*No.* 85.—Obtained by dissolving dry titanic acid in boiling $H_2SO_4$ and evaporating.

| | No. | Name. | System. | Form. | Double refraction shows colours of. | Direction of major axis. | Other optical characters. |
|---|---|---|---|---|---|---|---|
| TITANIUM. | | | | | | | |
| $Ti_2(SO_4)_3+3H_2O$ .. | 86 | | — | A resinous transparent yellowish deliquescent mass. | | | |
| $Ti_2(SO_4)_3+8H_2O$ .. | 87 | | — | Crystals in tufts. | | | |
| ZIRCONIUM. | | | | | | | |
| $Zr(SO_4)_2+4H_2O$ .. | 88 | | R | Spherulites, elongated lozenges, and six-sided micaceous-looking thin plates. Spherulites often constricted in the middle like dumb-bells. | 3rd order. | ∥ to *e*. Spherulites ∥ to axis of *Q.W*. | Absorption with single nicol. The elongated lozenges are deeply scored with numerous fine dark lines, which give them the appearance of bundles of micaceous plates. |

*Remarks.*

*No.* 86.—Is formed by the oxidation of the sesquisulphate with nitric acid and evaporating.

*No.* 87.—Is obtained by dissolving the metal in dilute $H_2SO_4$.

*No.* 88.—Swells up on heating with alum. Decomposes at a red heat.

(To be continued).

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## ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and J. B. MOYER.

WE proved in a former communication that mercury and bismuth cannot be separated electrolytically. These observations agree with those made by Smith and Salter (*Journ. Analyt. Chem.*, vii., 128), since they proved conclusively that copper and bismuth cannot be separated under corresponding conditions, and, further, that the assertion that bismuth and lead are separable under these conditions is incorrect.

### *Mercury from Lead.*

1. Ten c.c. of a nitric solution of mercuric oxide (=0·1150 grm. of metallic mercury), 1 c.c. of a nitric solution of lead (=0·0126 grm. lead peroxide), and 25 c.c. nitric acid of sp. gr. 1.3, were diluted to 175 c.c., and submitted to the action of a current giving 1·3 c.c. of detonating gas per minute. The mercury deposited weighed 0·1151 grm., and the lead peroxide 0·0123 grm. An examination of the mercury showed the absence of any admixture of particles of lead.

2. In this experiment the quantities of lead and mercury were the same as in 1; the volume of nitric acid was increased to 30 c.c., whilst the current indicated 1·8 c.c. detonating gas per minute. The deposit of mercury weighed 0·1150 grm. and the lead peroxide 0·0126 grm.

In three other experiments, in which the volumes of nitric acid (sp. gr. 1·3) added were respectively 5, 10, and 15 c.c.; the deposit of mercury contained metallic lead in varying but considerable quantities.

### *Mercury from Lead and Bismuth.*

In former communications we mentioned the analysis of an alloy of tin, mercury, lead, and bismuth, which Classen indicates (" Quant. Analyse durch. Electrolyse," 3rd edit., p. 147), and we showed that the analyst, if he pursues these instructions, will finally obtain very little bismuth, as beyond all doubt it will have been precipitated along with the mercury. Whilst disregarding tin, we submitted nitric solutions of the other three metals to the action of the current. The solution contained 0·1150 grm. mercury, 0·0126 grm. lead peroxide, 0·0718 grm. bismuth, and 15 c.c. nitric acid (sp. gr. 1·3), whilst the total solution amounted to 180 c.c. The current yielded 1·7 c.c. of detonating gas per minute. The deposit of mercury weighed 0·1262 grm., and the increase of weight of the anode was 0·0164 grm. Bismuth was found to have appeared at both poles.

A second and a third experiment, with an increased volume of acid, had a similar result. This process must therefore be rejected if a satisfactory separation is required.

### *Silver from Lead.*

The separation presented no especial differences in the two following experiments, if we work under conditions analogous to those given.

1. Ten c.c. of a nitric solution of silver (=0.1028 grm. silver), 1 c.c. nitric solution of lead (=0·0144 grm. lead peroxide), and 15 c.c. nitric acid (sp. gr. 1·3), with a total dilution to 200 c.c., were exposed to a current yielding 1·8 c.c. detonating gas per minute. The precipitate of silver weighed 0.1023 grm., and the lead peroxide 0·0144 grm.

2. The conditions as in No. 1. The precipitate of silver weighed 0·1028 grm., and the lead peroxide 0·0145 grm.

### *Copper from Cadmium.*

This separation was carried out successfully by Smith some time ago. Classen mentions similar results. Smith's method is described in the *Amer. Chem. Journal* (ii. 41). The following results confirm those of Smith in every respect:—

1. Ten c.c. of a sulphuric solution of cupric oxide (=0·1341 grm. Cu), 5 c.c. of a nitric solution of cadmium (=0·1 grm. Cd), and 5 c.c. nitric acid (sp. gr. 1·2), with a total dilution of 200 c.c., were submitted to a current which produced 0·6 c.c. of detonating gas per minute. The deposit of copper weighed 0·1346 grm., and contained no cadmium.

2. Under similar conditions as in No. 1 the precipitated copper weighed 0·1341 grm.

### *Copper from Zinc.*

The quantities of the metals were equal, the volume of nitric acid was 5 c.c. (sp. gr. 1·3), the total dilution 200 c.c., and the current gave 1 c.c. detonating gas per minute. The copper precipitated weighed 0·1345 grm. instead of 0·1341 grm.

### *Copper from Zinc, Cobalt, and Nickel.*

The quantities of the metals were equal, the volume of nitric acid 5 c.c. (sp. gr. 1·3). Total dilution 200 c.c. The current produced 0·4 c.c. detonating gas per minute. The precipitated copper weighed 0·1339.

### *Copper from Iron and Zinc.*

The metals were present in equal quantities. The volume of nitric acid was 5 c.c. (sp. gr. 1·3). The current 0·7 c.c. of detonating gas per minute. The total dilution was 200 c.c. The precipitate of metal weighed 0·1340 grm.

The copper in each of these operations was tested for the metals which had been jointly present, but which were all now wanting.

### *Bismuth from Cadmium,*

1. Five c.c. of a nitric solution of bismuth (=0·0718 grm. metallic bismuth), 5 c.c. of a nitric solution of cadmium (=0·1 grm. cadmium), and 15 c. c. nitric acid (sp. gr. 1·1), were diluted to 180 c.c., and treated with a current which gave 1·6 c.c. detonating gas per minute. The bismuth deposited weighed 0·0716 grm. instead of 0·0718.

2. The conditions of this experiment were the same as those of No. 1, with the exception that there was no further addition of acid to the nitric solution of the metals. The precipitated bismuth weighed 0·0719 grm.

### *Bismuth from Zinc.*

0·0718 grm. bismuth and 0·1 grm. zinc in presence of 2 c.c. nitric acid (sp. gr. 1·3), with a total dilution to 200 c.c., gave 0·0712 grm. bismuth, if treated with a current of 0·4 c.c. detonating gas per minute. The anode was slightly coloured, and its increase of weight was 0·0003 grm.

In a second experiment, with the addition of 1 c.c. of acid, the precipitated bismuth weighed 0·717. Hence we regard this separation as satisfactory.

### *Bismuth from Nickel.*

1. 0·0718 grm. bismuth and 0·1 grm. nickel in presence of 2 c.c. nitric acid (sp. gr. 1·3) were diluted with water to 180 c.c. and treated with a current giving 0·5 c.c. of detonating gas per minute. The precipitation of the bismuth was complete, and the deposit of metal weighed 0·0724 grm.

2. In this experiment the weights of metals were the same as in 1; the total dilution 200 c.c., the nitric acid 3 c.c. (of sp. gr. 1·3), and the current yielded 0·2 c.c. of detonating gas per minute. The deposit of bismuth weighed 0·0716 grm.

A third experiment, under exactly the same conditions, gave 0·0716 grm. bismuth. It contained no nickel, and no precipitate was observed on the anode.

### *Bismuth from Cobalt.*

The weights of the metals were 0·0718 grm. bismuth and 0·1 grm. cobalt. The nitric acid (spec. grav. 1·3) was 3 c.c., and the current gave off 0·2 c.c. detonating gas per minute. The precipitate of metallic bismuth weighed 0·0714 grm., and the anode was very slightly coloured. Further experiments showed that the separation is possible.

### *Bismuth from Zinc, Cobalt, and Nickel.*

0·0718 grm. bismuth, 0·1 grm. zinc, 0·1 grm. cobalt, and 0·1 grm. of nickel were mixed with 2 c.c. nitric acid (specific gravity 1·3), diluted to 200 c.c., and submitted to the action of a current which gave off 0·8 c.c. of detonating gas per minute. The deposit of bismuth weighed 0·0739 grm., and on examination it was found that both nickel and cobalt were present. The anode was covered with a blue film.

A second, third, and fourth experiment, under almost identical conditions, gave deposits of 0·0729, 0·0738, and 0·0739 grm. of bismuth, contaminated in each case with nickel and cobalt.

### *Bismuth from Cobalt and Nickel.*

Zinc was excluded in this experiment. The three metals were taken in the same proportions as above with 3 c.c. nitric acid (of specific gravity 1·3). The solution was exposed to a current which gave off 0·3 c.c. of detonating gas per minute. The deposit of bismuth weighed 0·0736 grm., and contained nickel.

### *Bismuth from Cobalt and Zinc.*

0·0718 grm. bismuth, 0·1 grm. cobalt, and 0·1 grm. zinc in solution were mixed with 2 c.c. nitric acid (specific gravity 1·3), and submitted to a current giving 0·6 c.c. detonating gas per minute. The bismuth weighed 0·0747 grm., and contained cobalt. The anode was covered with a film of oxide.

### *Bismuth from Cobalt, Nickel, and Zinc.*

On employing the same quantities of metals as in the above experiments, and increasing the nitric acid to 5 c.c. the precipitate of bismuth weighed 0·0728 grm., and contained both cobalt and nickel.

In an experiment under the above conditions we succeeded in separating all the metals present; 0·0718 grm. bismuth, 0·1 grm. zinc, 0·1 cobalt, 0·1 nickel, 8 c.c. nitric acid (specific gravity 1·3), total dilution 200 c.c., and a current which gave 0·4 c.c. detonating gas yielded a deposit of bismuth of 0·0718 grm. On examination the absence of the other metals was ascertained. The anode remained unaffected. Subsequent experiments were equally successful as regards the separation of the metals, though in some of them the anode appeared slightly coloured, its weight was not increased by more than 0·0004 grm.

The bismuth was deposited on platinum capsules of from 60 to 70 grms. in weight. In all the successful experiments the deposit was adherent and uniform. It was washed with warm water, alcohol, and ether. The strength of the current was ascertained by means of a voltameter, and the electrolyte was introduced in the circuit. The use of a nitric solution does not give such satisfactory results as the treatment of the metals in a sulphuric solution in presence of free sulphuric acid.—*Zeit. Anorganische Chemie.*

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 93).

Cd, No. 23, 231·35; No. 24, 226·55; No. 25, 219·45; No. 26, 214·41. Zn, No. 27, 209·88; No. 28, 206·10; No. 29, 202·43. Al, No. 30, 198·81; No. 31, 193·35; No. 32, 185·22. No. 28, No. 31, and No. 32 are double lines.

The photography of the cadmium spectrum formed the beginning of my investigation.

With a slit of the width of 0·020 m.m. and an exposure of one minute, the Leyden jar spark of cadmium gave all the main lines but the two most refrangible, No. 25 and No. 26, in contrast to the others, strikingly pale. As it might have been expected, this difference in intensity did not disappear, even on prolonged exposure, until solarisation became perceptible in the more intense lines. The difference in intensity which regularly followed on normal exposure would not have attracted my notice if I had not had at my disposal several cadmium proofs of extraneous origin—three original plates for which I am indebted to the kindness of Mr. W. N. Hartley, of Dublin—which have also been taken upon silver bromide gelatin with a quartz prism and quartz lenses.

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

These proofs showed the difference in the intensity of the above-named lines decidedly less than my plates. They therefore justify the assumption that Hartley's experimental arrangement had in some manner relatively assisted the photographic action of the lines No. 25 and No. 26. I was confirmed in this conclusion by three other cadmium photos. by the same spectroscopist; good photographic reproductions of which accompany one of his treatises (*Scientific Transactions of the Royal Dublin Society*, "Photos. of the Spark-spectra of Twenty-one Elementary Substances," vol. i., Series 2, pp. 231—238, 1882), and which, in contrast to the above named original plates, are in harmony with my plates; whence, therefore, the difference among Hartley's proofs? This question was of essential import for the continuation of my work.

Hartley, on the ground of the plates of his two negatives above named, had marked with a diamond the date 1880; his treatise appeared in 1882. My investigation began in the year 1889. As regards the arrangement in taking Hartley's plates above-mentioned, I merely know that an apparatus with quartz prisms had been employed. Hartley's treatise explained his arrangements in taking the other spectra. From reasons the exposition of which would prove tedious I have below, in the solution of the above question, kept myself exclusively to the proofs. This was admissible, since they display a difference palpable for the present case; the length of the spectra is different; if measured between the cadmium lines No. 9 and No. 26 it amounts in the plates to 82 m.m. and in the figures to 157 m.m. As both spectra show no appreciable difference in the re-solution of their crowded lines, it was permissible to assume that the dispersion of Hartley's spectral apparatus was the same, and that merely the focal distance of the lenses was different. Therefore the lengths of the aërial transit of the rays of both apparatus must have differed from each other approximately in the same proportion as the focal lengths. It has been already proved by Cornu (*D'Almedia J.*, x., pp. 5—17, 1881) that the transparency of the air decreases with the wave-lengths of the rays, especially in the ultra-violet, though certainly in strata of much greater thickness than those of Hartley's apparatus. Still, I have felt compelled to uphold the resistance of the air as the sole cause of the above named difference in the intensity of the two most refrangible lines of cadmium. On the one hand, because Miller's proofs already showed that a stratum of air, even of moderate thickness, may prove an insuperable difficulty in the photography of the ultra-violet; and, on the other hand, because all further experiments which I instituted to detect other causes for this phenomenon proved fruitless. An experimental strengthening of this assumption, the necessity for which seemed more urgent on every new photo, had to be postponed until the conclusion of the connected examination of the spectra of zinc and aluminium, on account of procuring the necessary instruments.

The zinc spectrum in its most refrangible part acted still more feebly than the cadmium spectrum. For instance, an exposure of three minutes was required for the appearance of the most refrangible line, No. 29. Like the efficacy, the intensity showed a further decrease. Of all the main lines of cadmium and zinc, none appeared so slightly as the zinc line No. 29. The combined spectrum of both metals showed better than any other that the intensity decreased with the wave-length as yielded by a spark springing over between these electrodes. (When employing three electrodes, I connect the pair of electrodes with the current-circuit, whilst the single electrode of the other metal was introduced with its extreme end into the track of the spark, where it then took part in the discharge in a normal manner). Few metals are here at all suitable like zinc and cadmium.

Contrasts in the intensity of adjacent ultra-violet lines are shown in the inflection spectrum better than in the refraction spectrum, since the deflection of the rays does not succeed progressively with the wave-length as with the prism, but proportionally. Hence the lines towards the more refrangible end are more and more crowded together, whilst in the refraction spectrum they recede further from each other. Proofs which I took with a concave grating revealed still better the decrease of the intensity and efficacy of the lines in question.

According to Cornu's hypothesis (*Comptes Rendus*, lxxxviii., pp. 1285—1290, 1879), a stratum of air of the thickness of 10 metres suffices for the absorption of the rays of the wave length 211·84 $\mu\mu$.

The rays Nos. 27, 28, and 29, the wave-lengths of which are smaller, are consequently absorbed by such a stratum of air in a still stronger degree.

(To be continued).

## THE SPECIFIC HEATS OF THE METALS.*

By JOS. W. RICHARDS, Ph.D.,
Instructor in Metallurgy, &c., in Lehigh University.

(Continued from p. 72.)

### Appendix.

### *Aluminum.*

[See a *résumé* on this subject by J. W. Richards, in *Journ. Franklin Institute*, February, 1892.]

First investigated by Regnault, in 1855, on very impure metal, obtaining 0·2056 between 25° and 97°, and, allowing for the impurities present, he made the figure for pure aluminum 0·2181. Had he used the correct specific heat of silicon in making this allowance he would have obtained 0·2200.

Investigated again by Regnault, a year after, on purer metal, obtaining a corrected value of 0·2143 (14°—97°),

Kopp used ordinary commercial aluminum, and obtained 0·2020 (20°—52°), as the mean of four determinations which varied from 0·1970 to 0·2070. This determination is, therefore, of very little value.

Mallet used chemically pure aluminum, and found by the Bunsen calorimeter 0·2253 (0°—100°).

Naccari (purity of metal not stated) investigated up to 300°, by the method of mixtures. His results lead to the formulæ—

$$S = 0{\cdot}2116 + 0{\cdot}000095\,t$$
$$Sm = 0{\cdot}2116 + 0{\cdot}0000475\,(t + t^{1}).$$

The mean 0°—100° would be 0·2164.

Richards used metal which analysed 99·93 per cent aluminum, the rest silicon. Temperatures pushed to 600°. Formulæ arrived at—

$$S = 0{\cdot}2220 + 0{\cdot}0001\,t$$
$$Q = 0{\cdot}2220\,t + 0{\cdot}00005\,t^{2}.$$

Mean 0°—100°, 0·2270, being less than 1 per cent from Mallet's value. The rate of increase with the temperature is similar to Naccari's observation. Total heat contained in the solid metal to its melting-point (625°), by this formula, 158·3 calories.

Le Verrier finds the specific heat between 0° and 300° to be invariable, and = 0·22; between 300° and 530° also constantly = 0·30; between 530° and 560° an absorption of about 10 calories rendered latent; between 540° and 600° the specific heat again constant and equal to 0·46. For the total quantities of heat in the metal he gives the following formulæ:—

Between 0° and 300° .. $Q = 0{\cdot}22\,t$
300° ,, 530° .. $Q = 65 + 30{\cdot}0\,(t - 300)$
540° ,, 600° .. $Q = 139 + 0{\cdot}46\,(t - 530)$.

Q becomes about 170 calories towards 600°, and rises rapidly, passing 200 before fusion at 620°.

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* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

Pionchon has recently published the following results:—

Between 0° and 580° .. $Q=0{\cdot}393\,t-\frac{291{\cdot}86\,t}{1517{\cdot}8+t}$

625° ,, 800° .. $Q=0{\cdot}308\,t-46{\cdot}9$.

Specific heat at 0°=0·2010; in the liquid state, above 625°, constant and equal to 0·308. He states that beginning at 580° the fusion starts, the metal losing its solidity, and between 623° and 628° the heat curve Q is nearly vertical. Pionchon's first formula gives for the total heat in the solid metal at the melting-point 160·49 calories.

*Latent Heat of Fusion.*—In 1890 the writer determined the amount of heat in solid aluminum as near as possible to its melting-point as 199·5 calories, and the heat in the molten metal as 229, from which he concluded that the latent heat of fusion was close to 30 calories. Since then two sources of errors have been disclosed in this determination.

(1.) The metal above 600° absorbs in advance some of its latent heat of fusion, the writer's observation in this regard agreeing with Le Verrier's, who states that the total heat exceeds 200 calories before real fusion occurs. If this phenomenon did not occur the writer's formula would give the heat content at the melting-point as 158·3, while Pionchon's formula gives 160·49, and it is these numbers which must be used in calculating the total heat absorbed during the change of state.

(2.) The heat in the molten metal at its setting-point is very greatly modified by impurities present. The writer found the following heats in impure and pure metal:—

| Per cent Pure. | Calories. |
|---|---|
| 96·9 | 229·0 |
| 99·9 | 254·0 |
| 99·93 | 258·3 |

The writer's results must then be considerably modified, in order to get the total latent heat. For the metal of greatest purity the total calculated absorption between 600° and 625°, due to change of state, would be—

258·3—158·3=100 calories.

Pionchon's formula for the heat in liquid aluminum evaluated for the meling-point gives 239·4 calories, and subtracting his lower value of 160·49 there is left 78·91 units as the latent heat. The writer's experiments would show that Pionchon's upper figure, 239·4, is probably nearly 20 units too low, since four experiments have given me 258·2, 258·9, 259·3, and 259·2 respectively.

### *Antimony.*

Prof. Wilcke gave 0·063; Crawford, 0·0645; Kirwan, 0·086.

Dulong and Petit give 0·0507 (0°—100°) and 0·0549 (0·300°), or in formulæ—

$$S=0{\cdot}0486+0{\cdot}000042\,t$$
$$Q=0{\cdot}0486\,t+0{\cdot}000021\,t^2.$$

F. E. Neumann, using commercial metal, found its specific heat by the method of cooling as 0·0470.

Regnault—

0·05077. (61°—97°).

Bède gives the formulæ—

$$S=0{\cdot}0466+0{\cdot}000040\,t$$
$$Q=0{\cdot}0466\,t+0{\cdot}000020\,t^2.$$

Kopp gives—

0·0523 at 31° (unreliable).

Bunsen—

0·0495 at (0°—100°).

L. Pebal and H. Jahn found the following mean values:—

Sm (−21° to −76°)=0·0496
Sm (−21° to − 0°)=0·0486
Sm ( 0° to −33°)=0·0495.

Naccari derives the formulæ—

$$S=0{\cdot}04864+0{\cdot}0000167\,t$$
$$Q=0{\cdot}04864\,t+0{\cdot}0000084\,t^2$$

### *Beryllium.*

Emerson Reynolds found 0·642 (20°—100°); while Nilson and Pettersson obtained 0·408 (0°—100°).

T. S. Humpidge investigated carefully through a range of temperatures, and gives the formula—

$$S=0{\cdot}3756+0{\cdot}00106\,t-0{\cdot}00000114\,t^2.$$

This formula evaluated for (0°—100°) would give 0·4248. It is therefore probable that Reynolds's value is much too high.

### *Barium.*

The Russian chemist Mendeléeff gives 0·05.

### *Bismuth.*

Prof. Wilcke made its specific heat 0·043.

Dulong and Petit found 0·0288, and Neumann 0·027 by the method of cooling.

Regnault made it 0·03084 (14°—99°).

Bède made experiments up to 200°, from which he calculated the formula—

$$Sm=0{\cdot}0269+0{\cdot}00002\,t,$$

which would give for (14°—99°) 0·0292, about 5 per cent lower than Regnault's result.

Kopp found 0·0305 (12°—60°), close to Regnault's figure.

Person found the specific heat of molten bismuth between 280° and 360° to be 0·0363.

*Latent Heat of Fusion.*—Dr. Irvine, Jun., determined that the latent heat would raise the temperature of 550 parts of solid bismuth 1° F., equal to 305·5 parts 1° C. He then assumed Wilcke's figure for the specific heat of bismuth which gives its latent heat as 11·92 calories. Had he used the specific heat found since by Regnault, his experiments would give 10·3. Or, had he used the specific heat at the melting-point as determined by Bède's formula, he would have obtained 10·8 calories.

Person made experiments with molten bismuth, from which he calculated that at its melting-point (266·8°) it contained 94·88 calories. But, assuming Regnault's value to be true to the melting-point for solid bismuth, the heat in solid bismuth is 82·24 calories, from which the latent heat of fusion is 12·64 calories. If, however, we take Bède's determination of its increasing 0·00002 for every degree rise in temperature, the mean specific heat to the melting-point would be 0·0322, the heat in solid bismuth at its melting point 86·00 calories, and the latent heat of fusion 8·88.

### *Cadmium.*

Regnault found 0·0567 (16°—98°) on metal containing 1 per cent of impurities.

De la Rive and Marcet found 0·0576, at ordinary temperatures, by the method of cooling.

Kopp found 0·0542 (15°—60°) method of mixtures.

Bunsen found 0·0548 (0°—100°) by the ice calorimeter.

Naccari experimented up to 300°, and gives the following formula:—

$$Sm=0{\cdot}0546+0{\cdot}000012\,t.$$

This evaluated for Regnault's range of temperature gives 0·0560.

*Latent Heat of Fusion.*—Person found 31·83 calories in molten cadmium at the melting-point (320·7°), and subtracting the heat in solid cadmium at that point, using Regnault's value, the latent heat of fusion became—

31·83 − 18·17 = 13·66.

Had he used Naccari's formula for the heat in solid cadmium he would have obtained 18·7, and for the latent heat of fusion 13·13.

### *Calcium.*

Bunsen found 0·1722 and 0·1686, mean 0·170 (30°—100°), by the ice calorimeter.

### *Cerium.*

Dr. W. F. Hillebrand gives 0·0448, at ordinary temperatures, determined on metal 95 per cent pure, allowing for the impurities, which were mostly iron and didymium.

### *Chromium.*

Kopp found 0·1000 (15°—60°); but since he found that of iron, with a larger atomic weight, to be greater than this, he concluded that this number must be too small, and supposed it due to the impurity of the material he was working with.

### *Cobalt.*

Dulong and Petit found 0·1498, by the method of cooling.

Regnault gives 0·10696 (13°—99°).

De la Rive and Marcet obtained 0·1172 as the mean of three experiments by the method of cooling. Regnault observes, however, that specimens containing carbon gave him as high as 0·117, but he took the smallest value as belonging to the purest metal.

Pionchon investigated up to 1160°. He found the specific heat at 0° to be 0·10584, his formula up to 900° being—

$$\mathrm{Sm} = 0{\cdot}10584 + 0{\cdot}00002287\,t + 0{\cdot}0000000219427\,t^2.$$

This formula evaluated for Regnault's range gives Sm (13°—99°) = 0·1086, about 15 per cent higher than Regnault's value. At about 900°, however, Pionchon observed a sudden change in the specific heat, so that above 900° the mean specific heat to 0° is expressed by the formula—

$$\mathrm{Sm} = 0{\cdot}124 + 0{\cdot}00004\,t - \frac{14{\cdot}8}{t}.$$

He could not definitely determine just how much heat was rendered latent in this change at 900°.

### *Copper.*

Wilcke found 0·114; Dr. Crawford, 0·1111; and Dalton gave 0·11, the latter by the method of cooling.

Dulong and Petit found 0·0949 (0°—100°) and 0·1013 (0°—300°), from which follows the formula—

$$\mathrm{Sm} = 0{\cdot}0917 + 0{\cdot}000032\,t.$$

Regnault gives 0·09515 (17°—98°); Dulong and Petit's formula evaluated for this range gives 0·09535.

Bède obtained a considerably lower result, giving up to 250°,—

$$\mathrm{Sm} = 0{\cdot}0910 + 0{\cdot}000023\,t,$$

which gives values at (15°—100°) about 2 per cent lower than Regnault.

Kopp obtained values between 0·0895 and 0·0949; average 0·0925 (15—60°).

Naccari worked up to 325°, and gives the formula—

$$\mathrm{Sm} = 0{\cdot}0921 + 0{\cdot}0000106\,t,$$

which gives, at 17°—98°, 0·0933. This result is almost the same as Bède's, but for higher temperatures would be much below his.

Le Verrier says that the specific heat of copper does not increase regularly with the temperature, but is constant between certain limits, that is,—

| | | | |
|---|---|---|---|
| Between 0° | and 360° | .. .. .. | 0·104 |
| 360° | „ 580° | .. .. .. | 0·125 |
| 580° | „ 780° | .. .. .. | 0·090 |
| 780° | „ 1000° | .. .. .. | 0·118 |

Further, that at the points where the changes occu- there is heat rendered latent, about 2 calories towards 350°, 2 calories towards 580°, 3·5 calories towards 780°. He states that the total heat in the copper is 117 calories towards 1020°.

In connection with Prof. B. W. Frazier, the writer has made a particular study of copper, reaching the conclusion that none of the above critical points occur, and that the specific heat increases regularly with the temperature according to the equations—

$$\begin{aligned} \mathrm{S} &= 0{\cdot}0939 + 0{\cdot}00003556\,t \\ \mathrm{Sm} &= 0{\cdot}0939 + 0{\cdot}00001778\,t \\ \mathrm{Q} &= 0{\cdot}0939\,t + 0{\cdot}00001778\,t^2. \end{aligned}$$

These formulæ were the true expressions of the results obtained up to 900°, and at none of the temperatures designated as critical points by Le Verrier were any deviations noticed. It would have been impossible for an absorption of 0·5 calorie to have occurred without having been detected. The ratio of the specific heat of copper to that of platinum throughout this range did not vary one-half of 1 per cent from 2·96, showing that the *ratio* of increase of specific heat with the temperature is the same in both metals.

*Latent Heat of Fusion.*—The mean value of six experiments on the amount of heat in molten copper at the melting point have given us 162·0 calories. The above formula evaluated for 1054° gives for the solid copper 118·7 calories. We have therefore determined the latent heat of fusion as 43·3 calories.

### *Didymium.*

Hillebrand obtained 0·04563 (0°—100°) in the ice calorimeter, allowing for 0·4 per cent of silicon, 0·3 per cent of iron, and 0·1 per cent of aluminum, which were in the specimen.

### *Gallium.*

Bettendorf obtained 0·079 (12°—23°) for solid gallium. Tomassi ("D'Electrochimie," p. 226) gives the specific heat of liquid gallium as 0·0802, and the latent heat of fusion as 19 calories. I do not know the name of the investigator who determined these.

### *Germanium.*

Nilson and Pettersson found the following mean specific heats:—

| | | |
|---|---|---|
| 0° to 100° | .. .. .. .. .. | 0·0737 |
| 0° to 211° | .. .. .. .. .. | 0·0773 |
| 0° to 302° | .. .. .. .. .. | 0·0768 |
| 0° to 440° | .. .. .. .. .. | 0·0757 |

As there is evidently first an increase and then a decrease, no simple formula can be derived to express these results.

### *Gold.*

Kirwan first made its specific heat 0·05; Dalton gave it as the same; Dulong and Petit obtained 0·0298 by the method of cooling.

Regnault obtained 0·03244 (12°—98°) with gold 999 fine. Violle worked with gold 1000 fine, and obtained for 0°—100° 0·0316. This is stated to remain sensibly constant up to 600°, and then to increase gradually towards the melting-point (1035°). At 900° Violle makes its specific heat 0·0345, and at 1020° 0·0352. It would appear from these figures that the specific heat of gold is more nearly constant, or rather changes less with the temperature than that of any other metal.

### *Indium.*

Bunsen has found with the ice calorimeter 0·0574 and 0·0565, mean 0·0570 between 0° and 100°.

### *Iridium.*

Regnault found 0·03672 (17°—98°), but remarks that the metal he used was impure.

Kopp obtained 0·0358 (15°—60°) with metal of greater purity.

Violle found for it exactly the same value as for platinum:—

$$\mathrm{Sm} = 0{\cdot}0317 + 0{\cdot}000006\,t.$$

He verified this formula up to 1400°. Violle further determined the heat in solid iridium just set as 84·2, 85·3, and 83·9 calories; mean 84·5, which, by the above formula, would indicate a maximum fusing-point of 1950°.

### *Iron.*

Wilcke gave 0·126; Crawford, 0·1269; Irvine, 0·143; Kirwan, 0·125; Dalton, 0·13; and Dulong, 0·11.

Dulong and Petit experimented up to 350°, obtaining the values—

| | |
|---|---|
| 0° to 100° .. .. .. .. | Sm = 0·1098 |
| 0° to 200° .. .. .. .. | Sm = 0·1150 |
| 0° to 300° .. .. .. .. | Sm = 0·1218 |
| 0° to 350° .. .. .. .. | Sm = 0·1255 |

which would lead to the formulæ—

$$Sm = 0{\cdot}1062 + 0{\cdot}000028\,t + 0\ 00000008\,t^2$$
$$S = 0{\cdot}1062 + 0{\cdot}000056\,t + 0{\cdot}00000024\,t^2.$$

It may be here remarked that all later investigators have reached similar formulæ of three terms, which means that the specific heat of iron increases more rapidly than the first power of the temperature. It should be borne in mind that these formulæ were verified only to 350°.

Regnault found 0·11352 (19°—98°), and, after the same piece had been heated to redness, 0·11380.

Bède obtained the following results:—

| | |
|---|---|
| 15° to 100° .. .. .. .. .. | 0·11230 |
| 16° to 142° .. .. .. .. .. | 0·11533 |
| 20° to 247° .. .. .. .. .. | 0·12331 |

From these observations he deduces the formula—

$$Sm = 0{\cdot}1053 + 0{\cdot}000071\,t,$$

but it can be seen from the data obtained that the value for 247° was higher than it should have been if the rate of increase had remained constant. A formula of three terms should, therefore have been derived to fit the data, and he should have given—

$$Sm = 0{\cdot}1050 + 0{\cdot}000065\,t + 0{\cdot}000000018\,t^2.$$

It will be observed that the coefficient of $t^2$ is smaller than in Dulong and Petit's formula, showing the curve to be nearer to a straight line.

Byström gives the true specific heat of iron, as deduced from his experiments, at every 50° up to 300°, as follows:—

| | | Differences. |
|---|---|---|
| 0° .. .. | S = 0·111641 | |
| | | 0·000728 |
| 50° .. .. | 0·112369 | |
| | | 0·001426 |
| 100° .. .. | 0·113795 | |
| | | 0·002154 |
| 150° .. .. | 0·115949 | |
| | | 0·002872 |
| 200° .. .. | 0·118821 | |
| | | 0·003590 |
| 250° .. .. | 0·122411 | |
| | | 0·004308 |
| 300° .. .. | 0·126719 | |

These data would lead to the formulæ—

$$S = 0{\cdot}11164 + 0{\cdot}00000718\,t + 0{\cdot}0000001436\,t^2$$
$$Sm = 0{\cdot}11164 + 0{\cdot}00000359\,t + 0{\cdot}0000000479\,t^2.$$

This formula differs from the previous ones in having a much larger value of the constant, a much smaller coefficient of $t$ and a larger coefficient of $t^2$, which is shown on the diagram by the curve starting higher, being quite flat for a distance and then rising rapidly. This formula evaluated for Regnault's range gives Sm (19°—98°) 0·1127, about 0·75 per cent below Regnault's value.

Kopp obtained results from iron, the average of eight experiments at 15° to 60° being 0·1120. His minimum value was 0·108, and maximum 0·114, showing here especially the roughness of his experiments and the general unreliability of his results, although the mean, in this case, comes very near the probably true value.

(To be continued.)

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 4, July 24, 1893.

**Researches on Samarium.**—Lecoq de Boisbaudran.—This paper will be inserted at some length.

**Density of Sulphurous Acid, its Compressibility, and its Expansion under Normal Conditions.**—A. Leduc.—The author finds the density of sulphurous acid = 2·2639.

**Oxidation of Nickel Sulphide.**—Ph. de Clermont.—The oxygen of the atmosphere cannot entirely oxidise the sulphur of this compound, and leaves a minimum quantity of nickel sulphide unattacked. This residue forms a fairly stable compound with the neutral sulphite.

**Crystalline Cuprous Phosphide.**—A. Granger.—The composition of this phosphide is $Cu_2P_2$. In appearance it is like graphite. It is attacked in the cold by chlorine and bromine. Dilute nitric acid dissolves it readily. If mixed with oxidising agents, such as potassium nitrate or chlorate, it detonates on percussion. If heated in contact with air it is oxidised and converted into copper phosphate. It is slightly soluble in hydrochloric acid; its solution gives with potassa a precipitate of cuprous oxide.

**Bismuth Sub-gallate.**—This compound is more generally known by its pharmaceutical name dermatol. Its composition is $C_7H_3O_5Bi.2H_2O$. In it bismuth oxide is combined with the acid function and the phenolic functions of gallic acid.

**Condensation of the Alcohols of the Fatty Series.**—A. Brochet and P. le Boulenger.—This paper does not admit of useful abstraction.

No. 5, July 31, 1893.

**Benzoylnicotine.**—A. Etard.—Benzoylnicotine is a colourless alkaloid, slightly viscid and having no tendency to crystallise. It is insoluble in water, and dissolves only in an excess of dilute hydrochloric acid. Its chloroplatinate, a light yellow crystalline precipitate, has the composition $[C_{10}H_{13}N(C_7H_5O)HCl]_2PtCl_4$.

**Fixation of Iodine by Starch.**—G. Rouvier.—If to known and equal volumes of starch water, the strength of which in starch is known, we gradually add larger and larger quantities of starch, there remains free iodine as soon as we pass the proportion $(C_6H_{10}O_5)_{16}I_3$.

**Preparation of Normal Caproic and Hexylic Acids.**—J. Tripier.—The oxidation of castor oil by a dilute mixture of sulphuric and nitric acids gives much more abundant yields than those obtained with nitric acid alone. The volatile products consist entirely of normal hexylic and heptylic acids, and a small quantity of pure heptylic nitrile.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 89.

**Report by Z. Roussin on M. Buisine's Memoir on the Purification of Sewage by means of Ferric Salts.**

**Purification of Sewage by means of Ferric Salts.**—M. Buisine.—The process described in these papers is thoroughly known in Britain.

## MISCELLANEOUS.

**The Cape Agricultural Journal.**—It is not often that an editor feels pleasure in acknowledging himself in the wrong. Such, however, is decidedly our case as regards our notice of the (Cape) *Agricultural Journal* inserted in Chem. News, vol. lxvii., p. 314. Our reviewer, being misled by the *names* of the analysts in question, supposed them to be aliens. Like ourselves, he is very glad to salute them as British subjects.

**Bibliography of Alcoholic Fermentation.**—The writer wishes to call the attention of fellow-workers to the fact that he is preparing a bibliography of alcoholic fermentation, with special reference to vegetable physiology. He will be very glad to receive notes concerning the literature of this question from botanists, chemists, and physiologists in this country who are interested in having bibliographies of this kind as complete as possible.—J. Christian Bay, Missouri Botanic Garden, St. Louis, Mo., U.S.A.

**A New Pathogenic Organism.**—At the recent meeting of the British Institute of Public Health, Edinburgh, Sir Charles A. Cameron, of Dublin, read a paper (by himself and Dr. McSweeney) on an organism isolated from a water which was supposed to have caused a local epidemic of enteric fever. The water proved to be polluted, and to contain a bacterium, which by culture proved to be intermediate between the *Bacterium coli communis* and the *Bacterium typhosum*. It resembles the latter in its cultivation on fuchsine agar, and its occasional exhibition of energetic mobility. It resembles the former in giving the indol reaction. In its mode of growth on potato it resembles closely *B. typhosum*, and in its energetic power of fermentation and its appearance on gelatin plates it resembles *B. coli communis*. This organism resembles in appearance both *B. typhosum* and *B. coli communis*; it is only by its behaviour under cultivation and its action on glucose, lactose, &c., that it can be differentiated from those bacteria. As it was found in water at Miltown, near Dublin, it may provisionally be termed the *Miltown bacterium*.

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SESSION 1893—94.

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SESSION 1893—94.

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THE CHEMICAL NEWS.
Vol. LXVII., No. 1761.

# ON THE ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

Beyond the simple statement found in most text-books, that the action of iodine and iodic acid, in presence of free alkali, on phenol results in the formation of the three mon-iodophenols together with a tri-iodophenol, little of importance seems to have been known until I. Messinger and G. Vortman reported on a new class of "iodine phenols" which they had obtained by modifying this reaction, which report appeared in the *Berichte Deut. Chem. Gesell.*, No. 12, 1889.

This latter class of "iodine phenols" have come to be of considerable importance, since some of them have been introduced into medicine, prominent amongst them being the article known as Aristol, which was originally introduced under the name annidalin. Messinger and Vortman studied the general reaction more minutely in order to found a volumetric method for the quantitative estimation of the phenols as a class, together with some allied compounds. This latter paper was published at a more recent date (1890) than the one referred to above and was abstracted by various English contemporaries. These abstracts originally attracted my attention to the subject, and to the British Pharmaceutical Conference Meeting of 1892 I contributed a paper, in which I dealt chiefly with the reaction as a method of assay, from a practical point of view, and in that sense criticised it. I was not then aware of the 1889 paper dealing with the composition of the compounds resulting.

In order to explain the large disappearance of iodine relative to the quantity substituted in the phenol molecule, I dealt very roughly with the probable composition of the compounds formed; my object being simply to show that the iodine percentages of the compounds were not commensurate with the consumption of iodine as found by titration, and more especially to show that where the greater consumption was indicated the compounds formed actually contained less iodine. I now propose to supplement that paper, to criticise other communications relative to the subject, to treat exhaustively a few typical cases, to deduce the *rationale* of the reaction in general, and prove the composition of a number of the compounds resulting. It must be borne in mind, however, that the substances as a class are of an exceedingly ill-defined nature, and therefore presented great difficulties in deciding whether a particular portion was a single substance or a mixture.

For the purposes of this paper, in estimating iodine the method of Carius was used throughout. Only one set of results will be given in each case. In the constitutional representations used throughout the following, the carbon atom symbols of the nuclei will not be inserted; and, indeed, such representations are used more because they show at a glance differences, than for any proved reason for choosing any particular structure.

## *Phenol* ($C_6H_6O$).

A quantity of the reddish violet precipitate was prepared as follows:—A solution containing 8 grms. phenol in 300 c.c. was prepared (solvent, water). 20 c.c. of this solution, together with 35 c.c. of normal solution of caustic soda, were diluted to about 1 litre, heated to 60° C., and decinormal solution of iodine run in to large excess, the whole allowed to stand for thirty minutes, and then acidified with dilute sulphuric acid. This process was repeated until a sufficient quantity was obtained.

Total iodine of this precipitate (air dried)—
Quantity taken =0·1584 grm.
Silver iodide found =0·2136 „ =72·85 p.c. iodine.

The precipitate was treated with cold ether as long as anything dissolved out, the ethereal solution was allowed to evaporate, and the residue recovered and powdered. This residue was of a yellowish brown colour, perfectly amorphous, resinous consistence, and readily fusible. The presence of iodine, other than that of substitution, being suspected, an attempt was made to drive it off by simple air heating, but fusion took place, accompanied with decomposition, and rendered this impossible. It was therefore placed in a tube together with metallic copper and water, sealed, and heated for a few hours at a temperature of about 120° C. The contents were then washed out, dried on water-bath, and dissolved out with ether. The recovered product was boiled with alcohol, and the alcoholic solution filtered off, the portion soluble in alcohol recovered and powdered. This was of a dirty white colour. It was dried in desiccator for two days, and finally at 50° C. in air-oven. It was then taken for analyses.

Total iodine of alcohol, soluble portion:—
Quantity taken =0·1660 grm.
Silver iodide found =0·2334 „ =75·96 p.c. iodine.

Combustion of same:—
Quantity taken =0·1276 grm.
Water found =0·0137 „ = 1·19 p.c. hydrogen.
Carbon dioxide found =0·0773 „ =16·52 „ carbon.
By difference .. .. = 6·33 „ oxygen.

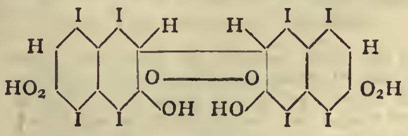
No very good formula can be derived from those analyses, probably owing to slight admixture, although it may roundly be represented thus, $C_{20}H_{12}I_9O_6$, showing that its constitution may be represented similarly to that of the following substance, assuming that one of the original benzene nuclei entering into its constitution had been, or became, tri-substituted, whilst only two of the original oxidised carbon atoms had become further oxidised.

The insoluble residue from the boiling alcohol treatment was dried; it appeared of a dirty white colour, and melted with decomposition (180° C.).

Total iodine of the alcohol-insoluble portion:—
Quantity taken =0·1002 grm.
Silver iodide found =0·1350 „ =72·79 p.c. iodine.

Combustion of same:—
Quantity taken =0·1312 grm.
Water found =0·0124 „ = 1·05 p.c. hydrogen.
Carbon dioxide found =0·0838 „ =17·42 „ carbon.
By difference .. .. = 8·74 „ oxygen.

Those results may be represented by the formula $C_{20}H_8I_8O_8$; or, constitutionally, thus—



Theoretical.
C=17·24
H= 0·58
I =72·98
O= 9·20

It is somewhat difficult to reconcile with theory the large percentage of hydrogen found without assuming the existence of hydrogen at the junction of the benzene ring, but this is extremely unlikely.

The remainder of the original precipitate insoluble in ether was treated similarly with chloroform, the chloroformic solution filtered, and the chloroform allowed to evaporate. The residue was of a bright violet-red colour, perfectly amorphous, and pulverulent. An attempt was made to free it from alleged loosely-combined iodine by treating with a weak alcoholic solution of caustic potash on the water-bath, but this was unavailing. The alcoholic potash was therefore filtered off and the residue washed. It was found that the potash had extracted a very small portion, readily fusible, which was thrown out on acidification. The quantity was too small for examination. The washed residue was heated with water and copper in sealed tube until decolorised, rinsed out, dried on water-bath, and dissolved out with carbon disulphide, recovered from the solvent and dried, then taken for analyses.

Total iodine :—

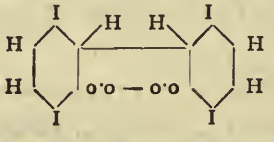
Quantity taken =0·1173 grm.
Silver iodide found =0·1507 „ =69·42 p.c. iodine.

Combustion of same :—

Quantity taken =0·1010 grm.
Water found =0·0103 „ = 1·13 p.c. hydrogen.
Carbon dioxide found =0·0748 „ =20·19 „ carbon.
By difference .. .. = 9·26 „ oxygen.

These results may fairly well be represented by the formula $C_{12}H_6I_4O_4$, although the iodine percentage is rather low, which might easily be accounted for by the heating at a high temperature in sealed tube, the carbon being correspondingly high.

It may be constitutionally represented thus :—



Theoretical :—
C=19·92
H= 0·83
I =70 36.

The remainder of the original precipitate insoluble in chloroform was treated similarly with carbon disulphide, in which it almost entirely dissolved, the carbon disulphide was evaporated off, and the residue which occurred in brittle scales—of a reddish violet colour—was powdered and dried. This latter residue constitutes the greater portion of the whole original precipitate. It does not fuse, but simply decomposes between 360° and 380° C. Any former portion of the original precipitate, extracted by a particular solvent in the order given, is also soluble in any solvent used for extraction after its removal. For instance, the whole precipitate is soluble in carbon disulphide. No part of the original precipitate is soluble in glacial acetic acid, whilst strong sulphuric acid only exerts a very slight solvent action on the more readily soluble portions.

Total iodine of the alcohol-ether-chloroform insoluble portion :—

Quantity taken =0·1840 grm.
Silver iodide found= 0·2485 „ =72·95 p.c. iodine.

Combustion of same :—

Quantity taken =0·2387 grm.
Water found =0·0161 „ = 0·75 p.c. hydrogen.
Carbon dioxide found =0·1797 „ =20·53 p.c. carbon.

A quantity of the same portion of precipitate was heated in sealed tube, together with copper and water, at a temperature of about 140° C., for three days. When taken out the red colour had disappeared, the suspected loosely combined iodine having been apparently eliminated. The mixture was evaporated to dryness on the water-bath, the dry residue washed with ether-chloroform and then dissolved out with carbon disulphide, the solution filtered and allowed to evaporate. The residue was again deposited in its scaly character, but now almost colourless. This was powdered, dried, and taken for analyses.

Total iodine :—

Quantity taken =0·3015 grm.
Silver iodide found =0·4009 „ =71·84 p.c. iodine.

Combustion of same :—

Quantity taken =0·1818 grm.
Water found =0·0141 „ = 0·86 p.c. hydrogen.
Carbon dioxide found =0·1402 „ =21·03 p.c. carbon.

A new batch of the red-violet precipitate was prepared and treated as before with ether, chloroform, and carbon disulphide in succession. A quantity of the carbon disulphide residue was air-dried, and the total iodine estimated.

Quantity taken =0·3418 grm.
Silver iodide found =0·4651 „ =73·52 p.c. iodine.

Another batch of the red-violet precipitate was prepared in presence of lead (in this case the colour of the precipitate was lighter).

The precipitate was separated by solvents as before, and a quantity of the carbon disulphide residue estimated for total iodine.

Quantity taken =0·23·76 grm.
Silver iodide found =0·3163 „ =71·08 p.c. iodine.

Another batch of the red-violet precipitate was prepared under the ordinary conditions, and the total iodine of the whole precipitate estimated.

Quantity taken =0·2073 grm.
Silver iodide found =0·2789 „ =72·69 p.c. iodine.

The total iodine percentages of the whole precipitates being so much less than those reported by Messinger and Vortman, namely, 78·95 and 79·70, a quantity was prepared, with a dilution equal to about an eighth of that used in the above preparations, and the iodine estimated.

Quantity taken =0·1238 grm.
Silver iodide found =0·1680 „ 73·32 p.c. iodine.

The differences may possibly be explained, by assuming that they had obtained mixtures containing larger quantities of a tri-substituted compound.

The quantity of "loosely-combined iodine" taken up is intimately connected with the quantity of free iodine existing in the mixture after the substances have all been satisfied, which fact can easily be demonstrated.

A new batch of the red-violet precipitate was prepared and separated as before. The alcohol-ether-chloroform insoluble portion, recovered from its solution in carbon disulphide, was taken for further experiment.

Total iodine :—

Quantity taken =0·1501 grm.
Silver iodide found =0·2111 „ =75·98 p.c. iodine.

A quantity of the same was heated together with water and copper in sealed tube, at a temperature of about 180° C., for three days. The product was then taken out, dried, and washed with ether and chloroform, then treated with carbon disulphide, the portion soluble in carbon disulphide recovered and dried. This was of the physical character as the similar product already treated of, and, like it, did not fuse, but decomposed on the temperature reaching about 360° C., carbon separating and iodine coming off free.

A small quantity of a dark greyish-brown substance remained, insoluble in carbon disulphide.

Total iodine of the carbon disulphide soluble portion :—

Quantity taken =0·2557 grm.
Silver iodide found =0·3400 " =71·84 p.c. iodine.

Combustion of same :—

Quantity taken =0·1935 grm.
Water found =0·0145 „ =0·83 p.c. hydrogen.
Carbon dioxide found =0·1547 „ =21·80 p.c. carbon.
By difference = 5 53 p.c. oxygen.

As the quantity of the greyish-brown insoluble part was so small, no satisfactory examination could be made of it; but an iodine assay and combustion were attempted, in order if possible to obtain some evidence of admixture of the original taken or some clue to the above discordant results:—

Total iodine:—

Quantity taken =0·0411 grm.
Silver iodide found =0·0342 ,, =44·96 p.c. iodine.

Combustion of same:—

Quantity taken =0·0460 grm.
Water found =0·0055 ,,
Carbon dioxide found =0·0212 ,, =12·57 p.c. carbon.
Ash (consisting chiefly of CuO and $Fe_2O_3$) =39·56 p.c.

This result, although valueless in itself, is of some use, in so far as it furnishes evidence that the portion retained by the copper was essentially of the same composition as the soluble portion, differing probably by its containing less oxygen. It also tends to dispel the possibility that the iodine percentages, although agreeing with those of the di-substituted compounds, were not really derived from mixtures of mono- and tri-substituted compounds.

A further quantity of the same separated portion as that used in the last series of experiments, together with a quantity of a previously "deiodised" portion (the quantity of material having become rather scant), were placed in a tube, together with water, finely divided silver, and copper, sealed, and heated for eight days between 180° and 200° C. The product was then taken out, dried, washed with ether-chloroform, and treated with carbon disulphide, which latter dissolved out the greater part of it. This soluble portion when recovered and powdered was of a light yellowish-white colour, and, like the other similar portions decomposed, without melting on the application of heat.

Total iodine of this portion:—

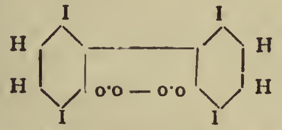
Quantity taken =0·2179 grm.
Silver iodide found =0·2859 ,, =70·89 p.c. iodine.

Combustion of same:—

Quantity taken =0·1152 grm.
Water found =0·0085 ,, = 0·81 p.c. hydrogen.
Carbon dioxide found =0·0848 ,, =20·07 p.c. carbon.
= 8·23 p.c. oxygen.

Those results answer well to the formula $C_{12}H_4I_4O_4$, although the analyses would indicate slight contamination with a similar compound of lower oxidation.

The compound may be represented constitutionally thus:—



Theoretical:—
C = 20·00
H = 0·55
I = 70·55

The remainder of the heated product, insoluble in carbon disulphide (cold), was boiled with successive quantities of carbon disulphide as long as anything dissolved out. The soluble part, which was very scanty, was recovered and dried, and the whole taken for iodine assay.

Total iodine:—

Quantity taken =0·0599 grm.
Silver iodide found =0·0643 ,, =58 p.c. iodine.

The fixed portion had evidently undergone decomposition.

(To be continued).

## ON THE DETERMINATION OF VANADIC ACID.*

(Continued from p. 77).

On the prolonged passage of carbonic acid through the solution, boiled and treated with sulphurous acid, a distinct oxidation of the vanadium tetroxide is perceived, occasioned by the air contained in the carbonic acid.

Arthur Rosenheim (Inaugural Dissertation, Berlin, 1888), in a research on vanadic-tungstic acid, has given communications on the determination of vanadic acid and its separation from tungstic acid.

Wolcott Gibbs (*Zeit. Anal. Chemie*, xxiii., 543), in the analysis of the vanadic tungstates, uses for separating vanadic and tungstic acids the process first employed by Berzelius, according to which the vanadic acid, after the decomposition of the vanadic-tungstic salt by prolonged boiling with ammonia, potassa, or soda lye, is eliminated as ammonium vanadate by means of a concentrated solution of ammonium chloride.

Rosenheim, in verifying this method, arrived at the following results:—

Vanadic acid is precipitated by ammonium chloride from very concentrated solutions of vanadates. Small quantities, however, as Roscoe has shown, remain in solution. If about 0·2 grm. of vanadic acid is used, there results a loss of about 0·3 per cent.

Tungstic acid is not appreciably precipitated by ammonium chloride, even from strongly concentrated solutions of tungstates.

The ammonium vanadate precipitated by ammonium chloride from mixtures of tungstates and vanadates occludes small quantities of ammonium tungstic. Larger quantities of vanadic acid remain in the solution, and the tungstic acid separated is converted on expulsion of the ammonium chloride into a black tungsten nitride not easily transformed.

Hence for accurate quantitative determinations, such as the analysis of vanadic tungstates, the separation of vanadic and tungstic acids by means of ammonium chloride is not available, as small quantities of vanadic acid are always present along with large proportions of tungstic acid.

For determining vanadic acid along with tungstic acid, Gibbs (*Zeit. Anal. Chemie*, xxiii., 543) has made use of a method depending on the circumstance that vanadic acid, whether free or combined, evolves chlorine if boiled with concentrated hydrochloric acid, and undergoes reduction. The free chlorine is determined in the usual method.

F. Mohr ("Lehrbuch der Titrirmèthode," 5th edition, p. 314) first pointed out this method; and Gibbs probably assumes, according to the statements of Mohr, that vanadic acid is reduced by hydrochloric acid according to the following equation:—

$$V_2O_5 + 2HCl = V_2O_4 + H_2O + 2Cl.$$

Rosenheim first sought to determine whether the reaction, in fact, ensues according to the above equation. To this end he studied the action of concentrated hydrochloric acid upon certain pure vanadates and upon pure vanadic acid.

From his experiments it appears that vanadic acid is never reduced by hydrochloric acid to $V_2O_4$ or one of its derivatives, and that consequently a volumetric method which depends on the above equation must give false results. There are probably formed some of the numerous oxides or their chlorine derivatives which lie between $V_2O_5$ and $V_2O_4$. The results of the numerous experiments do not justify us in establishing a fixed equation, and the method is therefore rejected by the author for quantitative determinations.

Attempts at founding a method of determining vanadic acid upon its behaviour with potassium iodide in a slightly acid solution had no better success.

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* *Zeitschrift fur Analytische Chemie.*

The volumetric method with permanganate is also applicable to the determination of vanadic acid along with tungstic acid.

According to the proposal of Gibbs (*Zeit. Anal. Chemie*, xxv., 544), the solution of the salts is first strongly acidified with a mixture of sulphuric acid and phosphoric acid in order to produce the phospho-tungstic acid which is not precipitable by acids; it is then reduced with sulphurous acid or hydrogen sulphide, and finally titrated with permanganate.

In testing this method the author arrived at the following results:—If vanadates and tungstates are simultaneously present the reduction of the vanadic acid takes place more slowly than in solutions of pure vanadates. The light blue vanadyl colour is masked by the violet-grey of the somewhat reduced phospho-tungstic acid. The transitions of colour in titration are modified, and the recognition of the permanganate colour is impeded.

For removing these difficulties the author dilutes the solution of the vanadic tungstate as far as possible. The more dilute the purer is the colour on reduction. When titrating, the flask should be set on a white support. The final reaction is recognised by a distinct reddish shine, which is visible by reflected light at the margin of the solution. When this reaction appears the level of the reagent is read off, and we ascertain by adding one or two more drops that the reaction is completed. The solution of permanganate should be very dilute. The author uses a solution 1 c.c. of which represents about 0·008 grm.

On observing the above precautions the results were very accurate, ranging between 100·05 and 100·18 per cent. The method is unexceptionable in the analysis of the vanadic tungstates.

(To be continued).

## STUDY OF CERTAIN NOVEL PHENOMENA OF FUSION AND VOLATILISATION PRODUCED BY MEANS OF THE HEAT OF THE ELECTRIC ARC.*

By HENRI MOISSAN.

(Concluded from p. 77).

*Silicon.*—With a current of 380 ampères and 80 volts we may effect the volatilisation of silicon. We find in the cold tube small spheres of silicon attackable by a mixture of nitric and hydrofluoric acids. These spheres are mixed with a grey dust and with a small quantity of silica. If we collect the vapours upon asbestos pasteboard we see that the chief part of the silicon has been converted into silica.

*Carbon.*—Duration of the experiment, twelve minutes; intensity of current, 370 ampères and 80 volts. If we heat under these conditions a crucible filled with coarse fragments of coke, all the mass of the latter is soon transformed into graphite. After the experiment we find in the cold tube thin, light, translucid plates of carbon of a maroon colour by transmitted light.

M. Berthelot in his numerous experiments on the progressive condensation of carbon has already indicated the existence of a light carbon of a maroon colour. This substance is separated by means of dilute hydrochloric acid from the lime, which has been volatilised at the same time. The residue thus obtained, which we are studying, burns readily in oxygen with the production of carbonic acid.

*Oxides.*—The researches which we have already indicated on the crystallisation of oxides demonstrate superabundantly the volatility of these compounds. We are about to show it for the oxides,—regarded heretofore as infusible,—lime, and magnesia.

*Lime.*—With a current of 350 ampères and 70 volts we effect the volatilisation of lime in from eight to ten minutes. Under these conditions we collect in the cold tube lime in the form of an amorphous dust presenting no spherules. Abundant vapours of calcium oxide escape from the furnace. With a current of 400 ampères and 80 volts the experiment is completed in five minutes. With a current of 1000 ampères and 80 volts 100 grms. of calcium oxide may be volatilised in five minutes.

*Magnesia.*—Magnesia is less easily volatilised than lime, and its boiling-point lies near its melting-point. When the magnesia is melted it emits vapours which may be condensed upon the cold tube. This experiment is effected with a current of 360 ampères and 80 volts. The distillation becomes very beautiful and rapid if we use currents of 1000 ampères and 80 volts.

In fine, at the high temperature of the electric arc both the metals and the non-metals, hitherto regarded as refractory, are volatilised. The most stable compounds of mineral chemistry disappear in the electric furnace either by dissociation or by volatilisation. Nothing remains to resist these high temperatures except a series of new, perfectly crystalline compounds of exceptional stability, the properties of which we shall soon describe. These are the borides, the silicides, and especially the metallic carbides.

M. Daubrée has already pointed out that the carbon of all our present organic compounds has originally existed in the state of metallic carbides. The electric furnace seems to realise the conditions of that remote geological epoch. It seems to us probable that these compounds may exist in the stars of high temperatures. At that same period the nitrogen would be found in the state of metallic nitrides, whilst the hydrogen was probably in a free state in a complex gaseous medium containing hydrocarbons and perhaps compounds of cyanogen.

## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.*

By Lieut.-General C. A. McMAHON, F.G.S.

(Continued from p. 80).

### PART III.

### *Aluminium.*†

Cæsium chloride is usually recommended as a test for the salts of aluminium, the reaction yielding cæsium-aluminium-alum (cubic); but inasmuch as CsCl itself crystallises in the cubic system, there is serious danger of the reagent being mistaken for the desired product. The sulphates of Cs or Rb are more suitable ($Cs_2SO_4$ is recommended), as they both crystallise in the rhombic system, and cannot therefore be mistaken for cæsium-alum. See Alum *ante*.

It is essential that samples of the sulphates obtained from the mineral under examination should be crystallised on glass slides prior to the addition of $Cs_2SO_4$ or $Rb_2SO_4$, in order to be sure that the mineral does not yield an alum without the addition of the reagent. When Mg as well as Al is present, as $MgSO_4$ forms monoclinic double salts with $Cs_2SO_4$ and $Rb_2SO_4$ (see Nos. 61 and 62, Part II.), sufficient of the reagent must be used to satisfy any $MgSO_4$ that may be present and leave sufficient over to convert the Al-sulphate into Cs- or Rb-alum. The advantage of $Cs_2SO_4$, or $Rb_2SO_4$, is that neither of these reagents forms alums with the sulphates of other metals (see Alums).

### *Barium.*

The sulphate of barium is almost insoluble in water

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* From the *Comptes Rendus.*

* *Mineralogical Magazine*, vol. x., No. 46, p. 79.

† The bases in Part III. are arranged alphabetically with reference to their *symbols*; soda, for instance, being under the letter N.

(1 in 400,000), and barium precipitated by $H_2SO_4$ has no crystalline form under the microscope. The sulphate, however, dissolves to a considerable extent in hot concentrated $H_2SO_4$, and deposits on cooling crystals having the composition—

$$H_2SO_4+BaSO_4, \text{ and } H_2SO_4+BaSO_4+2H_2O.$$

Very frequently both are deposited together, the character of the deposit depending a good deal on the condition of the atmosphere at the time. If the air is damp the hydrous salt may predominate; if it is dry the anhydrous salt may be the one principally found on the glass slide.

$$H_2SO_4+BaSO_4$$

is in microscopic four-sided* transparent crystals (*a*). One of the four sides is very commonly a little longer than the others, and this side is frequently curved inwards lik a concave lens. These small transparent crystals have straight extinction. More rarely crystals of hexagonal and more complex outline are formed. When the hot acid is exposed to a current of air, especially damp air, large skeleton crystals (*b*) are formed, which bear considerable resemblance to negative ice crystals. These are the skeleton forms of tabular rhombic crystals, and every transitional form up to a perfect rhomb may be seen. The skeletons extinguish in a line bisecting two arms. This is a very interesting fact, it seems to me, which throws light on the process of crystal building. Each molecule of these embryo crystals appears to be orientated not with reference to its present, but with reference to the ultimate form of the perfect crystals. Each molecule appears to have been endowed with what (for want of a better term) we must call polarity, and to have attached itself to its neighbour in a way that needed no subsequent modification as the mineral grew from a crystallite into a perfect crystal.† The fact that some embryo crystals of doubly refracting minerals show very little or no double refraction is, I think, due to the fact that owing to their excessive thinness they do not show colours between crossed nicols.

The sulphuric acid test is a delicate and sure one. It may be combined with ordinary testing in the following way:—Place some of the liquid to be tested in a test-tube or watch-glass. If $H_2SO_4$ gives a white precipitate, evaporate to dryness. Add concentrated $H_2SO_4$; heat for some time; draw off some of the clear, hot $H_2SO_4$ with a pipette, and place a few drops on a warm slide. If anhydrous crystals (*a*) be desired, allow the $H_2SO_4$ solution to cool gradually in a warm dry room. If the hydrous salt (*b*) be desired, allow the $H_2SO_4$ to cool in or near an open window or exposed to steamy air. If the preparation is to be mounted in Canada balsam, allow the slide to stand for twenty-four hours, then cautiously drain off the free $H_2SO_4$ with strips of filter paper.

2. If barium is present as sulphate I convert it into the chloride by the following process:—Evaporate solution to dryness; mix powder in agate mortar with sufficient charcoal to make the mixture dark grey in colour. Heat in small covered earthenware crucible strongly for one hour over a Bunsen burner. This converts the sulphate into the sulphide. Dissolve in dilute HCl, and heat until all the sulphuretted hydrogen is given off; fiter, evaporate to dryness; dissolve in water, and allow a few drops to evaporate on a glass slide. The crystals of $BaCl_2+2H_2O$ (*Monoc.*) thus obtained are in square prisms, very much resembling those of augite in shape. They almost always exhibit a very characteristic polysynthetic twinning, closely resembling the albite-baveno and albite-pericline twins of felspar. Two sets of these twins may sometimes be seen. Each set of multiple twins is apparently parallel to a pinacoidal face, and they intersect at about 90°. A third and fourth set may also be seen, which appear to be parallel to the prismatic faces.

3. With a solution of tartar-emetic barium chloride yields tabular rhombs with two acute angles of about 50° each. Sometimes one or both of the acute angles are cut off, giving six-sided forms. They extinguish parallel to a line bisecting the acute angles, and the major axis is parallel to that line. They polarise brilliantly in colours of the 1st and 2nd order. These crystals very commonly exhibit multiple twinning, the twinning plane being parallel to a line bisecting the obtuse angles of the rhomb.

### *Beryllium* (*Glucinum*).

The principal reaction mentioned in Clement and Renard's "Réactions Micro-chimiques" is the bichloride of platinum; but I do not think this is to be relied on when the beryllium to be tested is in the form of sulphate, for this salt and the chloroplatinate of beryllium both yield crystals belonging to the tetragonal system, and consequently one might be mistaken for the other.

1. The monoclinic salt may be obtained by dissolving the normal salt (tetragonal) in $H_2SO_4$. See Part II.

2. The double salt with $K_2SO_4$ is very characteristic. See Part II.

3. On the addition of KOH solution a precipitate of white flocculent $Be(OH)_2$ forms, which dissolves in an excess of the precipitant or on application of heat. A precipitate re-forms on addition of a few drops of ammonium chloride. The precipitate formed by KOH, on being allowed to crystallise spontaneously, deposits crystals of $K_2SO_4$ imbedded in $Be(OH)_2$. The latter appears in radiating sheaves, apparently monoclinic. Extinction 0°—25° to *e*, and this is also the major axis. Double refraction very high, reminding one of calcite.

4. By treating a solution of the sulphate with a solution of ammonium carbonate very remarkable crystals of beryllium carbonate may be obtained, which I think have not yet been described. If too much of the ammonium carbonate is used the mixture will yield a white, opaque, amorphous mass; if too little is used the result will be a structureless glass; but if the right proportion of the reagent is added a carbonate is obtained that gives crystals which resemble bivalve shells in a remarkable manner. This resemblance is increased by the fact that they project, sometimes standing up on edge, sometimes lying more on their sides, from a ground-mass of granular ill-formed crystals that look extremely like a matrix of broken shells. The large and perfect crystals have two discoidal faces (resembling the upper and lower valves of shells) joined by a sharp edge, which is very frequently truncated at one side in a way to simulate the hinge of a bivalve shell. Straight extinction—viz., ∥ to axis of elongation. Major axis ∥ to *e*. Between crossed nicols these crystals polarise in the blue of the 2nd order. Twinning is not uncommon. The combinations presented are varied. After mounting in Canada balsam the crystals gradually become more or less corroded.

5. The reagent recommended by Behrens is potassium oxalate, but the objection to this is that the results vary greatly with the proportion of the reagent to the beryllium salt. I obtained with one drop of the reagent a mass of globulites showing a cross under crossed nicols, and with from two to six drops: *a*, massive crystals; *b*, dendritic arrangements bristling with very sharply pointed spear-heads (rhombs with one of the acute angles projecting); *c*, lenticular crystals (with rather sharp terminations) shaped like a Zulu shield; and *d*, rosette-like groups of *c*, composed of two or more individuals. Extinction in *b* oblique; in *c* and *d* straight, viz., ∥ to *e*. Double refraction: *b*, *c*, and *d* polarise brilliantly in the blues and reds of the 2nd order. Refraction strong. I have not observed any twinning in *c* or *d*; the groups of crystals, *d*, are not in my specimens penetration twins, but thin plates overlapping each other.

### *Calcium.*

Gypsum ($CaSO_4+2H_2O$), the form in which the sulphate crystallises from aqueous solution under ordinary

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* By this and similar expressions it is intended that, as seen in transmitted light, the crystal has a four-sided *outline*.

† For another illustration of the same principle see Calcium (2).

conditions, is soluble in the proportion of 1 part in 500 parts of water at the ordinary temperature. The maximum solubility is attained at about 35°, after which it declines. I find in practice that by boiling powdered gypsum in water for from ten to fifteen minutes sufficient of the sulphate is taken up to give good typical crystals when a few drops of the solution are allowed to evaporate on a glass slide. The crystals usually lie on the 010 face, and are commonly elongated in one direction (apparently 110). Gypsum prisms are often very slender, and radiate from a common centre like the rays of a star. This grouping of slender needle-shaped prisms is very characteristic of the mineral, but it must not be accepted as conclusive evidence of its identity, as several other salts have a similar habit, and some of these have an oblique extinction similar to gypsum.

More important, to my mind, is the presence of very peculiar twins, which have always been present when I have allowed an aqueous solution to evaporate spontaneously on a glass slide. The re-entering angles appear to be formed by the prism faces (110), as a fibrous striping (110 cleavage) is very distinct on almost every twin crystal. Sometimes this has a curious resemblance to polysynthetic twinning. The twin crystals disappear when they are mounted in Canada balsam. Owing to their thinness, and the consequent feebleness of their double refraction, they rarely show even between crossed nicols.

Another very common and characteristic form is that of a prism. These prisms are usually isolated from other crystals, but sometimes they appear in combination with other forms. The major axis of elasticity is theoretically 37° 28′ from the axis of elongation, measured towards the acute angle of the rhomb, but it varies, I find, from 33° to 43°.

The above characteristic forms are often seen together on the same glass slide.

2. If a few drops of calcium sulphate in aqueous solution are placed on a glass slide, and a couple of drops of ammonium carbonate are added, the solution becomes clouded. On spontaneous evaporation numerous grains and congeries of grains of calcite are left on the glass. Long filamentous crystals, or strings of grains, are not uncommon, and these occasionally form skeleton rhombs, the obtuse angle of which varies from 105° to 108°. The high refraction and double refraction of calcite makes the detection of calcite crystals very easy. Being thin they usually polarise in brilliant colours. I have not succeeded in making magnesium carbonate in the above way, otherwise the latter might be mistaken for $CaCO_3$.

3. Concentrated $H_2SO_4$ raised to the boiling-point dissolves $CaSO_4$ to a certain extent, and deposits, on cooling, a salt which, according to Roscoe and Schorlemmer (vol. ii. [1], p. 203), consists "of microscopic prisms which have the composition $CaSO_4+H_2SO_4$." The results obtained by me are as follows:—A little of the hot acid solution allowed to cool slowly on a glass slide, and to stand for some time, deposits embryonic crystals consisting of round and oval disks and moss-like clumps, the latter of which, under high powers, are seen to be composed of spicules sticking out in all directions. More rarely microscopic crosses consisting of four arms and obscurely shaped crystals may be seen. Straight extinction, viz., parallel to the longer axis of the oval disks and to the arms of the cross. Major axis at right angles to the longer axis of the oval disks; relief good; the disks polarise in the yellow of the 1st order. The round disks in transmitted light are rather suggestive of silkworms' eggs; in reflected light they are a dull dead white.

Sometimes I have obtained a quantity of well-shaped crystals of the form shown at fig. 5 (see *Mineralogical Magazine*, x., No. 46); the sharp bows of these boat-shaped prisms meet at an angle of about 62°. At other times I have obtained crystals of the shapes shown at figs. 1 to 4. That at fig. 1 is not a thin platy crystal; but owing to the action of free $H_2SO_4$ on the balsam, and other causes, it is very difficult to make out the precise shapes of the side faces. Sometimes the top seems to be four-sided, and the side faces to be six-sided like the outline of fig. 5; but they cannot be made out exactly. All these crystals appear to belong to the orthorhombic system, and the mineral I doubt not is anhydrite ($CaSO_4$).

### *Cerium.*

Klement and Renard put in the foreground as tests oxalic acid and ammonium oxalate, but I have not obtained any very reliable results from these. I prefer ammonia as a test. This does not yield crystals, but its results are striking. If a drop of $CeSO_4$ solution is placed on a glass slide, and a drop of liquid ammonia is placed near it, the vapour from the latter, even when the drops are not allowed to touch each other, causes the $CeSO_4$ drop to assume a beautiful opalescent appearance. If the drops are allowed to evaporate side by side, or if ammonia be added to the $CeSO_4$, an isotropic deposit is formed which shrinks considerably as evaporation proceeds and becomes scored with cracks that give it the appearance of a slice of serpentine. When unmounted the dried deposit generally exhibits, like opal, a blue and red sheen.

2. With ammonium formate crystals of cerium formate, $Ce_2(CO_2H)_6$, are deposited in rounded, or six-sided, generally opaque white clumps, made up of micro-prisms which usually project from the edge of the mass. They have straight extinction. Direction of major axis doubtful. On mounting in balsam a few become translucent, and show colours up to the blue of the 2nd order. They look like radiating bunches of feathers, each feather with a central shaft and side barbs.

3. With $K_2SO_4$ (see Remarks, Part II.) cerous sulphate forms double salts. Under the microscope these form transparent hexagonal disks, microscopic crystals of complicated structure, some of which have pyramidal terminations, globulites, and irregular hexagonal disks made up of overlapping or irregularly grouped crystals. The apparently heterogeneous internal structure is increased by numerous inclusions of opaque matter. When the globulites are densely packed together so as to form an opaque crust, they often appear in reflected light like branching stalks of coral. Refraction high; double refraction never higher than blue of 2nd order.

4. With $Na_2SO_4$ and $Ce_2(SO_4)_3$ in the right proportion, we obtain small four-sided prisms terminated by sharp pyramids at both ends, or lenticular granules with sharp ends often arranged in groups like flowers with four petals. Extinction || to *e*. Major axis at right angles to *e*.

5. With potassium ferrocyanide, cerous sulphate yields (*a*) hexagonal disks; (*b*) short hexagonal prisms lying on their sides; and (*c*) stars with six rays, each star being an embryo hexagonal disk. The passage of the star into the hexagonal disk may often be seen, the almost complete forms being a hexagonal disk with a dark line running from the centre of each face towards the centre of the crystal. Other forms also occur, viz.—(*d*) four-rayed stars passing into; (*e*) short prisms of cube-like aspect; (*f*) bundles of bud-shaped crystals; (*g*) rounded complexes of small crystals suggestive of marigold flowers; and some variations of the skeletal form (*d*). (*a*) and (*c*) remain dark between crossed nicols; (*b*) and (*e*) have straight extinction; (*d*) polarises parallel to a line bisecting the rays of the star, and (*f*) to the axis of bundle. Major axis || to length of prism in (*b*) and at right angles to longer axis of (*f*).

### *Cobalt.*

1. If potassium nitrite solution be added to the aqueous solution of $COSO_4$, and then acetic acid to strong acid reaction, and the mixture gently warmed, a beautiful yellow precipitate (resembling the colour of chrome yellow) is formed. Under the microscope this yellow deposit ($K_6CO_2N_{12}+3H_2O$) is seen to be made up of very

small isotropic crystals in the shape of four-rayed stars or crosses with short arms. These are said to be the skeletons of crystals belonging to the cubic system. They require a 1-5th inch objective and 2nd eye-piece for their definition.

2. Solutions of cobalt that do not contain nickel, as an impurity, are said in Klement and Renard's work to give with oxalic acid the oxalate of cobalt ($CoC_2O_4+2H_2O$) in rectangular flat prisms (straight extinction), which are often grouped as rosettes, and one is referred to Plate VI., fig. 11, of their work for the form of these rosettes. Oxalic acid (straight extinction) itself, however, sometimes occurs in radiating groups of fine prisms exactly as those represented, and it seems possible that, in this case, the reagent may have been mistaken for the oxalate of cobalt. In my experiments this reaction has yielded white opaque globules with rough edges suggestive of a resemblance to the spores of ferns. Among these there are also numerous slender crystals of oxalic acid, some of which are in radiating star-shaped groups.

(To be continued.)

## THE SPECIFIC HEATS OF THE METALS.*

By JOS. W. RICHARDS, Ph.D.,
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(Continued from p. 85.)

### *Iron (continued).*

Naccari made experiments similar to Byström's, arriving at the formulæ—

$$S = 0{\cdot}1072 + 0{\cdot}000116\,t + 0{\cdot}0000001466\,t^2$$
$$Sm = 0{\cdot}1072 + 0{\cdot}000058\,t + 0{\cdot}0000000489\,t^2$$

The diagram shows clearly the relative position of Naccari's results.

Pionchon experimented up to 1150° with the soft iron of "Berry," which contained no manganese or phosphorus, and only a trace of carbon and silicon. Pionchon found two points at which heat was rendered latent, about 5·3 calories being absorbed between 660° and 720°, and 6·0 calories between 1000° and 1050°. He gives the following formulæ for the mean specific heat from temperatures within the designated limits to zero:—

$$(0° \text{ to } 660°)\,Sm = 0{\cdot}11012 + 0{\cdot}000025\,t + 0{\cdot}0000000547\,t^2$$
$$(660° \text{ to } 720°)\,Sm = 0{\cdot}57803 - 0{\cdot}001436\,t + 0{\cdot}000001195\,t^2$$
$$(720° \text{ to } 1000°)\,Sm = 0{\cdot}218 - \frac{39}{t}$$
$$(1050° \text{ to } 1160°)\,Sm = 0{\cdot}19887 - \frac{23{\cdot}44}{t}$$

It will be seen that the first formula is of the same nature as the preceding ones, the subsequent ones are complicated by having to include the heat rendered latent. The values of the true specific heat at any temperature are best seen by reference to the diagram. It increases gradually up to the first critical point, after which it remains constantly 0·218 until the second critical point is reached, after which it is again constant at 0·1989.

Pionchon remarks that these critical points coincide with sudden changes in the magnetic and conductive properties of iron, and also calls attention to the fact that from 720° to 1000° the specific heat is almost exactly double what it is at zero.

The presence of carbon and silicon in iron increase its specific heat, so that steel and cast iron are superior to pure iron in calorific capacity. The study of these bodies is therefore of interest, but can only be referred to briefly here. Regnault found the specific heat of cast steel (Haussman's) 0·11848, cast iron 0·12728, white iron 0·12983. Byström found that of cast steel 0·11850, and of pig iron 0·1283, and also found the variations of these with the temperature up to 300°; for full statement of which the reader is referred to his original paper.

### *Lanthanum.*

Dr. Hillebrand found 0·04485, using metal containing 4·6 per cent of didymium, 1·2 per cent of iron, 0·3 per cent of silicon, and a little aluminium, and calculating the allowance for these impurities.

### *Lead.*

Wilcke found 0·042; Crawford, 0·0352; Kirwan, 0·05; Dalton, 0·04; and Dulong and Petit, 0·0293; the last two by the method of cooling.

Regnault gives 0·03140 (15—98°).

Bède deduced from his experiments up to 200° the formula—

$$Sm = 0{\cdot}0286 + 0{\cdot}000019\,t.$$

This evaluated for Regnault's range gives 0·03075, two per cent below Regnault's value.

Kopp obtained 0·0308, 0·0302, 0·0293, and 0·0302; mean, 0·0301 (15—60°). Bède's formula gives for this range 0·0300.

Person found the specific heat of molten lead (335—430°) 0·0402.

Naccari experimented to 300°, and deduced the formulæ:—

$$S = 0{\cdot}02972 + 0{\cdot}0000136\,t$$
$$Sm = 0{\cdot}02972 + 0{\cdot}0000068\,t$$

This gives for Regnault's temperatures 0·03049, even a little below Bède.

Le Verrier finally states that the specific heat of lead is constantly 0·038 between 0° and 230°, that between 220° and 250° it is almost zero, for the metal absorbs almost no heat in traversing this interval of temperature, and between 250° and 300° the specific heat is constantly 0·0465. These results are so unexpected and differ at ordinary temperatures so greatly from Regnault's value (22 per cent difference), that we must conclude that they are quite improbable.

It is seen that there is some uncertainty as to the specific heat of lead at ordinary temperatures. On examining the diagram, it is seen that Bède's value for the specific heat increases until near the melting-point it is very nearly that observed by Person in the molten state. Now, since it has been observed in other metals that the specific heat in the solid state, near the melting-point, approaches the specific heat in the molten state, the writer is disposed to consider Bède's and Person's results as corroborating each other. I would, therefore, modify Bède's formula by using Regnault's value as affecting the constant, and write as the probably correct formulæ for lead—

$$Sm = 0{\cdot}02925 + 0{\cdot}000019\,t$$
$$S = 0{\cdot}02925 + 0{\cdot}000038\,t$$

This curve will pass through Regnault's value, and have the rate of increase determined by Bède.

*Latent Heat of Fusion.*—Dr. Irvine, jun., determined that the latent heat would raise the temperature of an equal weight of solid lead at the melting-point 162° F., and, using Crawford's value for the specific heat, this equals 5·6 calories F., or 3·1 C. If we use the value given by the above formula, 0·042415, his determination would give the latent heat as 3·8 calories.

Rudberg worked by the method of cooling also, and assuming that solid lead at its melting-point had a specific heat of 0·0352, he obtained 5·858 calories as the latent heat. If we use 0·042415 instead of 0·0352, the latent heat would become 7·058.

Person found molten lead at its melting-point to give out 15·61 calories. Assuming Regnault's value to be constant to the melting point, he obtained 5·37 calories as the latent heat. Had he used Bède's formula he would have obtained 4·27 calories, or with Naccari's formula 5·18 calories, or Bède's corrected formula 3·94. Or using the

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* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

*total* amount of heat in solid lead at its melting-point as found by Le Verrier (11·68 calories), the latent heat would be 3·93

I think the best conclusion to be drawn from this discussion is that the latent heat of fusion of lead is about this latter figure, 3·95 calories.

### *Lithium.*

Regnault gives 0·941 at 20—98°.

### *Magnesium.*

Regnault found 0·25 (22—98°); Kopp obtained results varying between 0·240 and 0·249; mean, 0·245 (15—55°).

### *Manganese.*

Regnault first found 0·1441 (14—98°), but remarked that the metal was impure. Afterwards he obtained 0·1330 with a specimen which showed important quantities of carbon and silicon. Still later he found 0·122 (12—98°) for a specimen containing still a little silicon.

### *Mercury.*

Crawford found 0·0357; Leslie, 0·0290; and Kirwan, 0·033. Dulong and Petit found 0·033 (0—100°) and 0·035 (0—300°), giving the formula—

$$Sm = 0{\cdot}0320 + 0{\cdot}00001\ t.$$

Regnault found 0·03332 (12—98°), and 0·0319 at −59°, in the solid state.

Winkelman found 0·03312 (20—50°), and 0·03278 (25—142°). This last result would indicate a decrease in the specific heat with rise of temperature, and lead to the formula—

$$S = 0{\cdot}0336 - 0{\cdot}0000069\ t.$$

Pettersson found—

| | |
|---|---|
| 0° to −5° | 0·033266 |
| −5 to −16 | 0·033262 |
| −5 to −26 | 0·033300 |
| −5 to −36 | 0·033299 |

Naccari has recently determined the following values for the true specific heat:—

| | |
|---|---|
| 0° | 0·03337 |
| 50 | 0·03310 |
| 100 | 0·03284 |
| 150 | 0·03259 |
| 200 | 0·03235 |
| 250 | 0·03212 |

These data show a regularly *decreasing* specific heat, and lead to the formulæ—

$$S = 0{\cdot}03337 - 0{\cdot}0000055\ t + 0{\cdot}000000002\ t^2$$
$$Sm = 0{\cdot}03337 - 0{\cdot}00000275\ t + 0{\cdot}00000000667\ t^2.$$

It will be noticed that Naccari's figures agree well with those of Winkelman, giving for 20—50°, 0·03322; and for 25—142°, 0·03309. Naccari's formula gives for Regnault's temperatures (12—98°) 0·03314, which is only 0·5 per cent different.

Milthaler has found as the mean of his experiments the formula—

$$S = S_0\,(1 - 0{\cdot}000138\ t)$$

If $S_0$ (the true specific heat at zero) be taken as 0·033266 (Pettersson's value) the formula becomes—

$$S = 0{\cdot}033266 - 0{\cdot}0000046\ t.$$

Or, if Naccari's value for $S_0$ is taken—

$$S = 0{\cdot}03337 - 0{\cdot}0000046\ t.$$

Or, if Regnault's value for S at 60° is taken—

$$S = 0{\cdot}033596 - 0{\cdot}00000461\ t.$$

If Petterson's results are reliable, they show that the specific heat of mercury between 0° and 36° is practically constant. The most recent experiments agree in showing that above 0° the specific heat decreases with the temperature.

Kundt and Warburg have determined the specific heat of vapour of mercury, which is found to be 0·1714 at constant pressure and 0·102843 at constant volume. Since these quantities are to each other in the proportion 5 : 3, it follows from the mechanical theory of heat that the molecule of mercury must consist of only one atom; a conclusion which agrees with that deduced from the density of mercury vapour, thus confirming in a remarkable manner one of the deductions from Clausius's theories.

*Latent Heat of Fusion and Vaporisation.*—Person found the latent heat of fusion by reversing the method of cooling, as 2·84 calories. Fabre and Silberman found the latent heat of vaporisation in an indirect way by means of iodine vapour as 77·5 calories.

### *Molybdenum.*

Regnault found 0·07218 (12—98°), but the specimen contained an undetermined amount of carbon.

De la Rive and Marcet found 0·0659 at ordinary temperatures by the method of cooling.

### *Nickel.*

Dalton found 0·10 and Dulong 0·1035, both by the method of cooling.

Regnault found 0·10863 (13—99°).

Pionchon investigated up to 1050°. He found a gradual increase in the specific heat up to 230°, but between that and 400° a very rapid increase, but after 400° the former rate resumed. He therefore concluded that between those two temperatures there is a gradual change of state, which would represent the absorption of 4·64 calories as latent heat. The diagram shows this break clearly. Pionchon gives the following formulæ for the mean specific heat to zero from any temperature within the designated limits.

Between—

0° and 230° $Sm = 0{\cdot}10836 + 0{\cdot}00002233\ t$

230 ,, 400 $Sm = 0{\cdot}183493 - 0{\cdot}000282\ t + 0{\cdot}000000467\ t^2$

440 ,, 1050 $Sm = 0{\cdot}099 + 0{\cdot}00003375\ t + \frac{6{\cdot}55}{t}$

Pionchon remarks that this change of state corresponds to known variations in nickel's magnetic and conducting properties.

Naccari experimented up to 320°, and deduces the formulæ—

$$S = 0{\cdot}1043 + 0{\cdot}0000946\ t$$
$$Sm = 0{\cdot}1043 + 0{\cdot}0000473\ t$$

Naccari remarks that all tests showed this metal to be pure, and that as far as he went he found no trace of the phenomenon mentioned by Pionchon.

### *Osmium.*

Regnault found 0·0311 (22—98°).

### *Palladium.*

Regnault gives 0·05928 (11—98°).

Violle investigated it up to 1265°, and found results agreeing to the formula—

$$Sm = 0{\cdot}0582 + 0{\cdot}000010\ t$$

This formula gives for Regnault's range 0·05929, a remarkable coincidence.

The amount of heat in solid palladium as near as possible to its melting-point was found to be 109·8 calories, which, according to the above equation, would indicate a maximum fusing-point of 1500°.

*Latent Heat of Fusion.*—Three experiments to find the heat in molten palladium at its setting-point gave 146·0, 145·8, and 146·4 calories respectively, mean 146·1. Subtracting from this the heat in solid palladium at that temperature leaves 36·3 calories as the latent heat of fusion.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, June 15th, 1893.*

Dr. Armstrong, President, in the Chair.

Mr. T. H. Easterfield was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Henry Ormsby Hale, B.A., Oundle School, Northamptonshire; Thomas Beilby Rawlins, 2, Leven Street, Pollockshields, Glasgow; Herbert Santer, Albion Brewery, Caledonian Road, N.; William Gilchrist White, Lamb Roe, Whalley, Lancashire; Edward Humphreys Winder, 37, Vincent Square, S.W.

The following were duly elected Fellows of the Society:—John Bateman, Henry Bailey, Douglas T. C. Berridge, Robert S. Cahill, John Henry Coste, S. W. M. Davy, Arthur Henry Green, Ernest Albert Hancock, James John Howitt, John Walter Leather, Alexander Mitchell Martin, Charles Mills, Charles Alexander McKerrow, K. P. McElroy, John Watson Napier, William Ridgely Orndorff, Alexander Orr, George Ritchie, Wilfred Sessions, Henry Thomas Sorrel, Frank Ernest Thompson, Claude Theodore Vautin, Edward Augustus Warmington, Thomas Whittaker, Sydney Whally.

Of the following papers those marked * were read:—

*33. "*Contributions to our Knowledge of the Aconite Alkaloids.* Part VI. *Conversion of Aconitine into Isaconitine.*" By Wyndham R. Dunstan, M.A., F.R.S., and Francis H. Carr.

In a previous communication it has been shown that the roots of *Aconitum napellus* contain, besides the highly poisonous aconitine, an almost non-poisonous isomeride —isaconitine. These alkaloids are evidently intimately related, as both furnish aconine and benzoic acid on hydrolysis. The authors now show that when an aqueous solution of aconitine hydrobromide (m. p. 163°) is heated, change very gradually takes place, the isomeric *isaconitine hydrobromide* (m. p. 282°) being produced. The change is facilitated by the addition of a small quantity (1—2 per cent) of hydrogen bromide, but is not assisted if sufficient is present to induce hydrolysis of a large proportion of aconitine. The isaconitine was identified not only by the high melting-point of its salts, but also by the formation and analysis of the characteristic auchlorisaconitine. No similar change could be detected in the case of aconitine nitrate, either when neutral or acid solution was used, nor could the conversion be effected by heating aconitine with glacial acetic acid, although in this case anhydraconitine is produced if the heating be continued during eighteen hours at 120°. Aconitine may be dissolved in concentrated sulphuric acid, and the solution gently heated without the conversion into isaconitine taking place; nor does aconitine sulphate undergo conversion into the isomeride when it is heated many hours in contact with very dilute sulphuric acid. No isaconitine seems to be produced during the hydrolysis of aconitine by cold soda solution. The authors are making further experiments in the hope of gaining information with regard to the mechanism of the conversion of aconitine hydrobromide into isaconitine hydrobromide.

*34. "*Contributions to Our Knowledge of the Aconite Alkaloids.* Part VII. *Some Modifications of Aconitine Aurichloride.*" By Wyndham R. Dunstan, M.A., F.R.S., and H. A. D. Jowett.

Certain irregularities having been observed in the melting-point of aconitine aurichloride,—

$$C_{33}H_{45}NO_{12},HAuCl_4$$

(see Part I.) prepared under different conditions from pure aconitine, the subject was fully investigated, the result being that three distinct isomeric modifications have been isolated differing in melting-point and crystalline form.

When auric chloride is added to a solution of aconitine hydrochloride, a yellow amorphous precipitate is thrown down, from which directly or indirectly the three crystalline modifications can be obtained by employing different solvents. *Aconitine α-aurichloride* is most readily produced in rosettes of needles by crystallisation from a mixture of acetone and water, or less readily and certainly in rectangular plates from dilute alcohol. The crystals melt at 135·5°. When re-crystallised from strong alcohol, this compound changes into the β-modification.

*Aconitine β-aurichloride* is obtained by crystallising from strong alcohol. It forms rosettes of needle-shaped crystals which melt at 152°. When this substance is re-crystallised from a mixture of chloroform and ether it changes into the γ modification, and when re-crystallised from a mixture of acetone and water it appears as the α-modification.

*Aconitine γ aurichloride* cannot apparently be formed directly from the amorphous precipitate or from the α-aurichloride. It is, however, easily prepared by re-crystallising the β-aurichloride from a mixture of chloroform and ether, when it separates in prisms melting at 176°. When crystallised from strong alcohol, this substance is converted into needles of the β-aurichloride; and on crystallising it from a mixture of acetone and water, the α-modification is obtained. When the β- and γ-modifications are melted they pass into the α aurichloride. From each of the modifications one and the same crystalline aconitine (m. p. 188—189°) may be recovered. They behave, then, as true "physical" isomerides, no chemical difference being detectable between them.

*35. "*Note on the Stereoisomerism of Nitrogen Compounds.*" By S. U. Pickering.

Hantzsch and Werner's suggestion that the isomerism of some triad nitrogen compounds may be explained by referring them to a tetrahedron and assuming that the nitrogen occupies one corner instead of the centre is tantamount to representing one side only of the nitrogen atom as capable of entering into combination. It leads to further difficulties when the nitrogen becomes pentad, as, in order to preserve the tetrahedral form, the nitrogen atom has to be placed in the centre of the tetrahedron together with one of the monad atoms. An alternative explanation which has been offered is based on the supposition that the isomerides are produced according as one of the bonds of the nitrogen atoms inclines towards one or other of the groups in its vicinity, an explanation for which the study of compounds of other elements affords no justification. In suggesting an arrangement of atoms in space, our ignorance of the matter renders the simplest possible arrangement the only justifiable one. This, in the case of an atom combining with three or five others, is that three of these should be arranged in one plane at equal distances around the central atom, the other two being placed in a plane at right angles, so that each of them is equidistant from the first three. This arrangement, though not symmetrical, is the most nearly symmetrical one possible. It affords, in the author's opinion, a perfect explanation of the stable character of ammonia derivative, and of the fact that in ammonium derivatives two of the group can be very easily split off. It explains the isomerism found in the hydroximes and hydrazones by one of the groups present being united by different bonds in the two cases (two of the five bonds being always free), just as in the isomerism of carbon compounds, and it agrees well with the facts as to isomerism and optical activity observed in the case of ammoniom derivatives. Moreover, as the nitrogen atom can form a symmetrical compound with any two, as well as with three, of its bonds occupied, it also affords an explanation of the existence of nitric oxide and peroxide.

*36. "*A Study of the Properties of Some Strong Solutions.*" By S. U. Pickering.

The depressions of the freezing-points of the three solvents water, acetic acid, and benzene by a number of non-electrolytes (methyl, ethyl, and propyl alcohols, diethylamine, pyridine, ethyl ether, carbon bisulphide, acetic anhydride) were examined, the determinations being extended to the strongest solutions possible. The results showed that the slight irregularities which are observable in the results afforded by weak solutions become one of the most marked features in the case of strong solutions, and any theory which attempts to explain the nature of solutions while ignoring the existence of these irregularities must necessarily be imperfect. The nature of the dissolved substance has an obvious effect on the character of the results, but it is impossible to ascribe this character to the nature of the dissolved substance only, as the peculiarities exhibited by a particular substance in one solvent are often absent when another solvent is used; these peculiarities would appear to be explicable only on the assumption that every solution contains substances peculiar to itself—*i.e.*, compounds of the solvent and substance—and does not consist merely of the juxtaposed free solvent and free substance.

In the various series, 29 breaks were observed in the regions embracing fairly simple molecular proportions (1 : 4 to 4 : 1 mols.), and of these, 24 agree within experimental error with molecular proportions, the remaining 5 being breaks whose existence or position was doubtful. Additional evidence is thus afforded as to the existence and significance of these breaks, and their occurrence is shown not to be confined to cases in which the solvent is water.

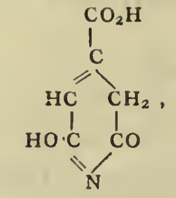
*37. "*Studies on Citrazinic Acid.*" By W. J. Sell and T. H. Easterfield.

A new method of preparing citrazinamide is described, which consists in fusing a mixture of citric acid and urea. The alkali salts of the amide and the normal and acid alkali salts of the acid are described, and an account is given of trichlorcitrazinic acid and its behaviour with phenylhydrazine.

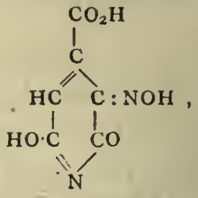
The authors find that the production of a blue colour when citrazinic acid is warmed with dilute solutions of potassium nitrite is due to the formation of a quinhydroketopyridine, a substance whose alkaline solution has an intense blue colour; this, however, is only the final stage of a series in which isonitrosocitrazinic acid is first formed. The isonitroso-compound is very unstable; it is oxidised by nitric or nitrous acid and converted into a stable yellow acid of the formula $C_6H_2N_2O_5 \cdot 4H_2O$; hence, if an excess of nitrite be employed in applying the colour test for citrazinic acid, no blue colour results. The yellow acid is dibasic, and its solutions precipitate potassium or ammonium salts from solutions of the chlorides of those metals.

By the action of dilute sulphuric acid or of reducing agents, isonitrosocitrazinic acid is converted into $\alpha\beta'$-quinhydro- and $\alpha$-ketopyridine, which crystallises in lustrous, bronze-green coloured prisms. The same substance may be produced by reducing the yellow acid. The quinhydrone is easily converted by oxidation into the corresponding quinone, which resembles ordinary quinone in many of its properties, and may be re-converted by sulphurous acid and other reducing agents to the quinhydrone. On reduction the quinhydrone gives a colourless solution which probably contains the quinol, as, on exposure to air, the liquid begins at once to deposit crystals of the quinhydrone; the quinol has not yet been isolated.

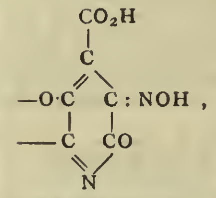
A bright red-coloured phenylhydrazocitrazinic acid, corresponding to the above isonitroso-derivative, is obtained by the action of diazobenzene chloride on citrazinic acid; this substance forms characteristic salts. The following formulæ are provisionally suggested for the substances described:—



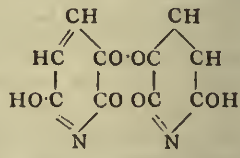
Citrazinic acid.



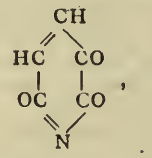
Isonitrosocitrazinic acid.



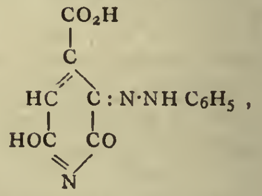
Yellow acid, ½ mol.



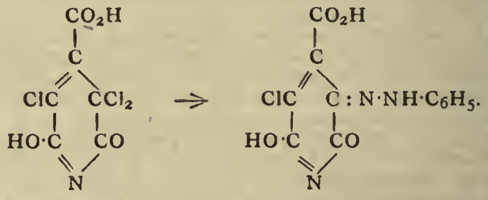
Quinhydroketopyridine.



Quinoketopyridine.



Phenylhydrazocitrazinic acid.



Trichlorcitrazinic acid.

Chlorphenylhydrazocitrazinic acid (as salts).

Discussion.

Dr. Kipping said the published statements regarding citrazinic acid agree in assigning to it the property of fluorescence, which, according to Dr. Armstrong's views on the origin and nature of colour, it should not possess, assuming it to have the usually accepted constitution. At Dr. Armstrong's suggestion, Mr. O. F. Russell and himself undertook to settle, if possible, this question of fluorescence, and for this purpose they prepared citrazinic acid by two methods, of which that described by Behrmann and Hofmann was found to give the better results, the acid obtained by Ruhemann's process from ethylic acetyl citrate being difficult to purify.

A freshly-prepared alkaline solution of the crude product is highly fluorescent, but when the acid is carefully purified by converting it into the ethylic salt and crystallising the latter from acetic acid, this is no longer the case. A small quantity of pure citrazinic acid dissolved in concentrated soda gives a colourless solution without visible fluorescence; on shaking for a few minutes in contact with air a slight but gradually increasing blue fluorescence is observed, caused doubtless by the presence of some oxidation or decomposition product of the acid. A solution containing pure ethylic citrazinate, together with sodium carbonate, becomes fluorescent on exposure to the air, but apparently more slowly than a solution of the acid.

Some further experiments were made with citrazinic acid with the object of elucidating its constitution. Ethylic citrazinate gave with acetic anhydride a colourless crystalline diacetyl derivative, $C_{12}H_{13}NO_6$, the composition of which was determined by the ordinary methods and by direct estimation of the quantity of acetic acid produced on decomposition with sulphuric acid. Attempts to prepare a hydrazone and a hydroxime from citrazinic acid were unsuccessful. By suspending citrazinic acid in water and passing nitrous fumes into the ice-cold mixture, a substance of the composition $C_6H_6N_2O_6$, which is evidently identical with the authors' isonitrosocitrazinic acid, was obtained; this compound can be obtained in almost colourless crystals by recrystallisation from ethylic acetate and petroleum. The action of potash and methyl iodide on citrazinic acid seems to be quite abnormal, but the nature of the product, which was of an uninviting character, was not determined. Citrazinic acid combines with dry bromine, yielding a crystalline substance which is readily soluble in water and ethylic acetate; it is, however, unstable, and loses hydrogen bromide very readily, being converted into a yellowish powder which is practically insoluble in ethylic acetate.

*38. "*The Essential Oil of Hops.*" Preliminary Notice. By Alfred C. Chapman.

About 80 kilos. of hops, some of which had been grown in Burgundy, some in Alsace, and the remainder in Kent and Sussex, were submitted to steam distillation in quantities of about 1 kilo. at a time.

When the greater part of the oil had been prepared the author was compelled, owing to pressure of other work, to discontinue its examination. and it was placed aside in a well-stoppered bottle, which it filled; at the end of about ten or eleven months, the remainder of the oil (about 30 c.c.) was prepared, and the whole was then twice steam-distilled to free it from resin; about 140 c.c. were obtained. On submitting the oil to distillation it commenced to boil at 170°, the thermometer rapidly rising to 230°, the greater part distilling over between 230° and 270°. After several fractionations, finally over sodium, about 40 c.c. of oil were obtained, boiling between 256° and 261° (uncorr.). This was found, on examination, to be a sesquiterpene, three combustions giving numbers closely agreeing with those required by the formula $C_{15}H_{24}$.

Two vapour density determinations by Hofmann's method gave 6·91 and 7·1, the vapour density required by $C_{15}H_{24}$ being 7·1. The boiling-point of the sesquiterpene corrected for the emergent mercurial column was 261 to 265°. Its relative density was found to be 0·8987 at 15°/15°, and 0·8955 at 20°/10°; when examined in a tube 100 m.m. long at 20°, it produced a rotation of 1° 5′ to the right, corresponding to a specific rotatory power of +1·2°.

Its index of refraction for the red hydrogen line, *h*H*a*, was 1·4978, corresponding to a specific refractive energy of 0·555.

Another freshly-distilled sample of hop oil, which was examined soon after its preparation, was found to boil at much lower temperatures, and consisted of lower boiling-point terpenes, together with an oxygenated constituent, and contained but little of the sesquiterpene. It is proposed both to continue the study of the sesquiterpene and to examine in detail the other constituents of oil of hops in the hope of gaining some insight into the nature of the changes which occur during the ageing of the essential oil.

*39. "*The Sulphides and Polysulphides of Ammonium.*" By W. P. Bloxam.

After calling attention to the uncertain state of our knowledge of the changes which solutions of ammonia saturated with hydrogen sulphide undergo when oxidised by exposure to the air, the author describes qualitative experiments, from which he infers that in addition to polysulphide such solutions contain *thiosulphate*, but never more than traces of sulphite, and that no sulphate is produced. These conclusions are based on the application of the method of testing recommended by Fresenius ("Qual. Anal.," Eng. trans. of 15th German ed., p. 193), using cadmium chloride in place of zinc chloride to remove sulphides, as this proved to be a more effective agent, but adding the latter salt, as its presence was found to be essential to the production of the colouration characteristic of sulphite. It is pointed out that the presence of excess of ammonia enhances the delicacy of the test for sulphite.

In order to follow with success the changes undergone by solutions of "ammonium sulphide" on oxidation, the author has endeavoured to prepare the various sulphides and polysulphides in a pure state, and describes the results of a large number of experiments. In analysing the solutions of ammonium sulphides, the total sulphur was determined after oxidation by alkaline hypobromite; to determine the polysulphide sulphur, the solutions were boiled with excess of chlorhydric acid to expel sulphuretted hydrogen, and the residual sulphur was then oxidised by hypobromite, &c.; ammonia was estimated by boiling with excess of standardised chlorhydric acid, and then determining the amount of acid in excess.

A concentrated solution of ammonia ($d=0·880$) does not absorb the amount of hydrogen sulphide required to convert the whole of the ammonia into sulphydride, $NH_4·SH$, a solution saturated at air temperature taking up only about 75 per cent of that amount, and having a composition which may be represented by the formula $(NH_4)_2S·2NH_4·SH$. Less concentrated solutions of ammonia absorb a larger proportion of hydrogen sulphide, a mixture of one volume of ammonia solution (0·880) with four volumes of water taking up sufficient to form a solution of the composition corresponding with the formula $NH_4SH$, the strongest solution of this substance which is obtainable containing only about 16 per cent. The author infers, however, from the results obtained on passing hydrogen sulphide into various mixtures of water and ammonia solution cooled with ice water, that the solutions do not progressively take up more hydrogen sulphide as they become weaker, but that the amount absorbed is constant within certain well-defined limits, viz.:—

| Ammonia sol. | : | Water. | Composition of sol. |
|---|---|---|---|
| 3 | : | 1 | $(NH_4)_2S,4NH_4·SH$ |
| 2 | : | 1 | $(NH_4)_2S,8NH_4·SH$ |
| 1 | : | 1 | $(NH_4)_2S,8NH_4·SH$ |
| 1 | : | 2 | $(NH_4)_2S,18NH_4·SH$ |
| 1 | : | 3 | $(NH_4)_2S,18NH_4·SH$ |
| 1 | : | 4 | $NH_4·SH$ |

The author attributes this remarkable behaviour to the actual formation of double sulphides, and states that he has obtained several such in crystals. Thus, by cooling, the solution having a composition corresponding with the formula $(NH_4)_2S·2NH_4·SH$, crystals of this composition were obtained; whereas a concentrated solution of ammonia, saturated at air temperature with hydrogen sulphide, then cooled to 0° and further saturated with the gas, gave highly hydrated crystals of the formula—

$$(NH_4)_2S·12NH_4·SH;$$

and a concentrated solution of ammonia, cooled to 0° and then saturated with hydrogen sulphide, gave well-defined crystals, the composition of which is represented by the formula $(NH_4)_2S·18NH_4·SH$.

What appears to be ammonium sulphydride, $NH_4·SH$, may be obtained in the solid state by passing the two gases into a vessel surrounded with ice, the hydrogen sulphide being maintained in slight excess; compounds of the type $(NH_4)_2S·xNH_4·SH$ are also formed if the ammonia be in excess.

By exercising great care in adjusting the volumes of the two gases and the rate of flow, operating at 18°, micaceous crystals are obtained, which, when rapidly dissolved in ice-cold water, yield a solution the composition of which sufficiently approximates to that required by the formula $(NH_4)_2S$ to justify the conclusion that they consist of this compound; but if a large excess of ammonia passes through the bottle, a more volatile sulphide is obtained in the form of an oil, which appears to be a compound of the formula $(NH_4)_2S{\cdot}2NH_3$.

When an alcoholic solution of ammonia is saturated with hydrogen sulphide, crystalline compounds of the formula $(NH_4)_2S{\cdot}xNH_4{\cdot}SH$, containing alcohol of crystallisation, are obtained, the value of $x$ depending on the concentration, as in the case of aqueous solutions.

The formation of definite polysulphides appears to be attended with considerable difficulty; "ammonium sulphide" solutions dissolve, at most, the amount of sulphur required to form a polysulphide of the formula $(NH_4)_4S_9$, and the author is inclined to regard the simpler polysulphides as secondary products resulting from the decomposition of this compound or of analogous lower compounds.

(To be continued.)

## CORRESPONDENCE.

### OZONE.

*To the Editor of the Chemical News.*

Monsieur,—Je suis français, et non italien. Déjà, lors de la publication de mes articles dans *l'Electrical Review*, le "Microbe phylloxera," s'était glissé dans un paragraphe que je traduisais de Fröhlich; on a justement critique l'expression; j'ai soigneusement fait la correction et malgré cela, le "Microbe phylloxera" a reparu dans la brochure. Ce n'est pas moi qui ai suggiré l'extermination du Phylloxera et la purification des Eaux d'égoût par l'ozone, c'est le Dr. Fröhlich.

Quant aus microbes inoffensifs qui si trouvent dans des endroits infectés par des microbes dangereux, si l'ozone les tue, ce n'est pas mafaute, c'était à eus de ne pas fréquenter mauvaise compagnie, et ils ont le soir des autres.

Agréez mes remerciements pour votre critique bienviellante.

E. Andreoli.

18, Somerleyton Road,
12 Aout, 1893.

### BRITISH ASSOCIATION ANNOUNCEMENTS.

*To the Editor of the Chemical News.*

Sir,—Many of your readers will be interested to know that M. Moissan has kindly undertaken to arrange a demonstration of the properties of fluorine for a meeting of the Chemical Section of the British Association, at Nottingham, in September next.

We hope also to have at least two important discussions—one on Bacteriological Work, and the Chemical Problems connected with it; the other on Explosions in Coal Mines, with special reference to the Dust Theory. Professor Percy Frankland will open the former discussion and Professor Harold Dixon the latter.

It would be a considerable convenience to the Organising Committee if chemists, physicists, or biologists who wish to take part in the discussions and to contribute papers will be so good as to send an early intimation to the Secretaries, Burlington House.—I am, &c.,

J. Emerson Reynolds.

University of Dublin, Trinity College,
August 21, 1893.

**Constitution of the Di-cyanides of Di-molecular Acids.**—L. Bouveault.—The cyanides of di-molecular acids are substituted $\beta$-ketonic nitriles. If they present an analogous reaction they may be transformed into monoximes of triketones, the analogues of which are only found in the aromatic series.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 14.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 6, August 7, 1893.

**Origin of Atmospheric Oxygen.**—Dr. T. L. Phipson.—The substance of this paper has already been inserted as a communication from the author.

**Isomorphism in the Anhydrous Alums.**—T. Klobb.—The anhydrous alums, as well as the corresponding hydrated compounds, are isomorphous, and crystallise together in all proportions. Their crystalline form is that of a regular hexagonal prism. It is difficult to decide if this form is simply pseudo-hexagonal. These conclusions have been verified on the one hand for the oxides $Cr_2O_3$, $Al_2O_3$, $Fe_2O_3$, and on the other hand for $K_2O,Na_2O(NH_4)_2O$.

*Bulletin de la Société Chimique de Paris.* Series 3, Vols. ix. and x., No. 14.

**Fixation of the Group = $CH_2$ in Certain Amidic Derivatives.**—A. Trillat.—It must be supposed from analogy that when formaldehyd acts upon an amidic substance, in which only a single hydrogen is free, two mols. of this substance enter into combination.

**A New Series of Colouring Matters.**—A. Trillat.—The author describes derivatives of rosaniline, of sulphorosaniline, chrysaniline, $\beta$-amidoalizarine, and the azo-derivatives.

**Some Acetones Derived from Acrylic Acid.**—Ch. Moureu.—The author has obtained and described phenylvinylacetone, $C_6H_5{-}CO{-}CH{=}CH_2$.

**Soluble Gums.**—Pietro Palladino.—The author has published a complete monograph of the gums of commerce with reference to their use in medicine, their falsifications, their constitution, and their origin. Tables are given which summarise their behaviour with iodine, oxalic acid, ammonium oxalate, ammonia ferric chloride, borax, albumen, nitric acid, ammonium molybdate, basic lead acetate, potassa, orcine, orceine, mercurous nitrate, stannous chloride, potassium silicate, tannic acid. To detect dextrine the author heats the sample to ebullition for a minute with aniline sulphate, chlorobrucine, pure brucine, orcine, or orceine. With these reagents gum, in an alkaline solution (KOH), gives a pale straw colour, which sometimes becomes a little greenish, whilst gums containing dextrine take a yellowish orange or a brownish red colour.

**Preparation of Silver Monedate.**—E. J. Maumené.—In this paper, which is not suitable for abstraction, the author gives silver formiate the name "silver monedate," whilst the oxalate is spoken of as monaedate.

**The Chromosulphuric, Chromodisulphuric, and Chromotrisulphuric Acid and the Chromosulphates.**—A. Recoura.—Already noticed.

**Determination of the Fixed and Volatile Acids of Wines.**—J. A. Müller.—This paper will be inserted at length.

**Salts of Diamidophenol (Orthopara 1.2.4) and Triamidophenol 1.2.4.6**—A. Lumière and A. Seyewetz.—Not adapted for abstraction.

**Phenylallylcarbinol.**—H. Fournier.—The author finds that a procedure similar to that of Saytzeff may be generalised for the preparation of the secondary alcohols of the aromatic series.

**Action of Zinc and Magnesium on Metallic Solutions and on the Determination of Potassa.**—A. Villiers and F. Borg.—This paper will be inserted in full.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1762.

ON THE
# ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 89).

When the red-violet precipitate is prepared in presence of lead a considerable proportion of the resulting precipitate remains insoluble on treatment with carbon disulphide and contains a large quantity of lead. A similarly insoluble portion is obtained frequently containing the metals iron and calcium if the solution in which the precipitation takes place contains a relatively large proportion of those metals in an available condition. One would be naturally inclined to the opinion that such metals existed in a state of true chemical combination, but from various experiments made in this direction I think that the combination is at most of a very loose molecular kind—of the metal oxide with the compound. All attempts to prepare a metal compound approaching saturation failed.

A quantity of such "lead compound" was treated as follows:—

Weight of crucible .. .. .. =7·5225 grms.
" " + substance =7·6203 "

Substance taken .. .. =0·0978 "

The crucible with substance was then heated in a mercury bath to about 340° C. until the substance had almost lost its maroon colour, which colour is due to the "loosely-combined iodine" which I have already proved.

| | Grms. |
|---|---|
| Weight of crucible + substance after heating .. | =7·6176 |
| " " " before " .. | =7·6203 |
| Iodine lost .. .. .. .. .. | =0·0027 |
| | =2·8 p.c. |

Total iodine of original:—
Quantity taken =0·0974 grm.
Silver iodide found =0·1068 " =59·24 p.c. iodine.
∴ 56·44 is equal to the percentage of true substituted iodine (approx.).

Combustion of the heated portion:—
Quantity taken =0·0869 grm.
Water found =0·0071 " = 0·90 p.c. hydrogen.
Carbon dioxide found =0·0488 " =15·31 p.c. carbon.
Ash (chiefly PbO with a trace of silica).. .. .. .. .. =13·35 p.c.

*Attempted Reduction of the Alcohol-Ether-Chloroform Insoluble Portion of Red-Violet Precipitate Soluble in Carbon Disulphide.*

In this case it was also treated with boiling chloroform prior to solution in carbon disulphide. The carbon disulphide solution was placed in a stoppered vessel, together with a quantity of a solution of caustic soda and treatment with sodium amalgam, carried on for a period extending over five days. The mixture quickly assumed a muddy appearance and lost its red colour. As the reaction proceeded the magma became stiffer, the addition of water making little difference. The aqueous layer ultimately assumed a yellowish brown colour. The whole mixture was then thrown into a large volume of water and shaken up. The brown watery solution was filtered off and the operation repeated a number of times, a dark brownish watery solution being obtained each time, whilst a considerable volume of gas escaped after each shaking. The brown aqueous washings were acidified, when the brown colour disappeared, giving place to a yellowish milky fluid having a fetid penetrating odour. The milky-looking fluid was shaken up with ether, which extracted nearly all the visible substance; the ethereal solution was then shaken up with a solution of caustic potash, into which the substance passed. This operation was repeated a second time. During this transaction a black caoutchouc-looking substance fell out which contained mercury. The alkaline solution was evaporated, and a small quantity of needle-shaped crystals were obtained mixed with a quantity of a dark brownish non-crystalline substance, from which the crystals were separated and washed.

The crystals (a sulphur determination only could be made):—
Quantity taken = 0·0732 grm.
Barium sulphate found = 0·0536 " =10·06 p.c. sulphur.

This result furnishes the evidence required, since the percentage of sulphur found is sufficient to show that the compound could only contain one atom of sulphur to two benzene nuclei; thereby confirming the existence in the original of the di-phenol molecule, which has been assumed throughout the constitutional representations already given, largely on account of their analogy with the thymol compounds yet to be considered.

The blackish coloured insoluble mass which was filtered out from the brown aqueous solution was treated with ether, when a yellowish solution was obtained having a particularly fetid odour. The remainder was then treated with carbon disulphide, which dissolved out a considerable portion.

*The Ethereal Solution.*—This was shaken up with a weak solution of caustic potash, when a portion passed into the solution (alkaline), whilst another yellowish coloured portion separated out solid at the junction of the fluids, not soluble to any extent in one or the other. This was separated and washed. When washed and dried it was of a yellowish white appearance and brittle; it did not melt, and was quite odourless.

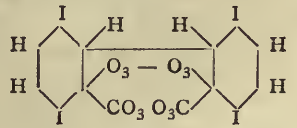
Total iodine of this insoluble portion:—
Quantity taken =0·0961 grm.
Silver iodide found = 0·1011 " =56·84 p.c. iodine.

Combustion of same:—
Quantity taken =0·1218 grm.
Water found =0·0116 " = 1·05 p.c. hydrogen.
Carbon dioxide found =0·0830 " =18·58 p.c. carbon.
Ash = 3·40 p.c.
No sulphur.

Allowing for ash we would have per cent:—

$$C=19·19,\ H=1·10,\ I=58·71,\ O=21·00,$$

which may be represented by the formula $C_{14}H_6I_4O_{12}$, and admitting this to be true might be represented constitutionally thus:—



Theoretical:—
C = 19·22
H = 0·68
I = 58·12.

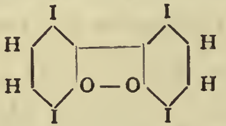
This would, indeed, appear to be a somewhat startling product to be taken from a reduction mixture, but it must be remembered that the carbon disulphide had also entered into the reaction. However as this may be, I have no reason to doubt the analyses, and, indeed, the iodine percentage was controlled by a check experiment, but as further confirmatory work outlay the line of this research I merely give the data.

The portion dissolved out by the carbon disulphide when recovered was of a whitish colour and brittle scaly character.

Total iodine of this portion :—
Quantity taken =0·1644 grm.
Silver iodide found =0·2217 ,, =73·47 p.c. iodine.

Combustion of same :—
Quantity taken =0·1184 grm.
Water found =0·0098 ,, = 0·92 p.c. hydrogen.
Carbon dioxide found =0·0921 ,, =21·21 p.c. carbon.
By difference .. .. = 4·4 p.c. oxygen.

Those results may be represented by the formula $C_{12}H_4I_4O_2$, and constitutionally thus—



Theoretical :—
C =20·93
H= 0·58
I =73·83

(To be continued).

## NEW METHOD FOR THE PRODUCTION OF SODIUM AND POTASSIUM FERROCYANIDE.

By H. N. WARREN, Research Analyst.

The alloy now known as zinc-eisen, and which at the present time is largely used in pyrotechny, the which has already been briefly described by the author in subsequent pages of this journal, will be remembered is produced by the action of ferrous chloride upon metallic zinc; giving rise to a brittle regulus of zinc, containing up to 15 or 20 per cent of iron. The same compound, in return, is now being experimented with as a reducing agent for the sulphocyanides.

The potassium or sodium salt, as the case may be, is procured by the action of ammonia upon carbon disulphide dissolved in petroleum. If this mixture is kept below 212° F., there is produced ammonium sulphocarbamate, which, if briskly boiled for a short time, is resolved into ammonium sulphocyanate; this being afterwards converted into its equivalent of either potassium or sodium salts by the introduction of either of those bases; the ammonia thus evolved being collected in the usual manner and employed in a further operation.

If the calcined sodium or potassium salt thus prepared is intimately mixed with an equivalent proportion of the zinc alloy and heated to redness, the sulphur present is gradually absorbed by the zinc, whilst the iron remains for the production of the ferrocyanide. The mass thus obtained is lixiviated and evaporated; the ferrocyanide crystallising out as the liquid cools, which may be further purified by re-crystallisation.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

**Crystalline Basic Copper Seleniate and an Analogous Salt of Cobalt.**—M. Bogdan.—The salt in question has the composition $2SeO_3,3CuO,4H_2O$. It forms very small crystals insoluble in water and freely soluble in air. At 250° they are decomposed, losing water and selenium, which forms a reddish deposit on the cold parts of the tube. The cobalt salt has the composition $3SeO_34CoOH_2O$. It forms red acicular crystals, which, if heated, behave like the corresponding salt of copper.—*Bull. de la Soc. Chim. de Paris*, ix.-x., No. 14.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 82).

I utilised this fact in order, even before the completion of the above-named new apparatus (see *ante*), to procure a more certain basis for the measurement of the absorption of the more refrangible rays in the air than was afforded by the former observations. To this end I executed some proofs with the quartz apparatus, in which the sparks and the photographic plate were distant from each other, not 10, but 17 metres. The light was conducted directly into the apparatus. Two quartz lenses placed at the focal distance of the rays arriving at the plate in front of the slit and the sparks co-axially with the collimator, collected these rays in the aperture of the slit of the collimator. After fifteen minutes' exposure all the zinc lines appeared, contrary to expectation, although very thin and devoid of expression, which, however, was this time unimportant. The important part of the result was the fact that the atmospheric air, as tested by brom-silver gelatin, is far more pervious to light than might have been expected according to Cornu. In addition, the thickness of the stratum of air employed by no means corresponded to the limit of transparency. According to my firm conviction a much thicker stratum of air would have led to the same result. How did my assumption of the influence of the air upon the photographic efficacy of the most refrangible rays agree with this result? Little as I could bring them in harmony, the cadmium phenomena furnished ground enough to uphold them unaltered. That the numerical values which Cornu has given for the aërial absorption could no longer serve as a basis after they had been found doubtfully trustworthy in my photographs of the zinc spectrum need not surprise us. Cornu's statements are founded on the behaviour of the wet collodion plate, whilst my proofs were taken only with the gelatin plate. The sensitiveness of both plates is fundamentally different, and in that part of the spectrum which exclusively concerns us it is totally unknown. How the sensitiveness of both plates may vary in the ultra-violet we have hitherto no observations to show.

I next proceeded to take the spectrum of aluminium. The first experiments were fruitless. Not until I had enlarged the slit to the unusual extent of 1½ m.m. and had exposed for twenty minutes did I succeed for the first time in recognising on the fixed plate at least traces of the line No. 30 and the less refrangible components of the double line No. 31. The image of lines was certainly so faint that under ordinary circumstances it was visible neither by transmitted nor by reflected light. To perceive it distinctly especial precautions are required. In the same manner I subsequently obtained, after an exposure of forty-five minutes, the remaining aluminium lines. Thus I had arrived at the region of the smallest wave-lengths, but had by no means attained my purpose. My proofs certainly supplied evidence that the most refrangible aluminium rays after traversing a stratum of air of 2 mètres in thickness could still exert upon silver-bromide gelatin an impression capable of development; but an application of such proofs in spectroscopy, at which I was aiming, was not to be thought of. The clearness of the lines was insufficient.

An attempt to obtain better results by elevating the energy of the rays failed completely. What I effected with an induction apparatus of unusual size, constructed by Keiser and Schmidt, of Berlin (length of sparks 50

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

c.m.), expressly for these proofs, demonstrated merely that the object could not be approached in this direction.

More for the sake of completeness than with a hope of success I executed an aluminium proof with the above-mentioned grating apparatus. I never obtained even a trace of a line. The grating was well suited for taking the zinc lines, but with the aluminium lines of the shortest wave-length it failed entirely.

Nothing remained but to take a photograph with a thicker air stratum. After I had studied the behaviour of my plate in the aluminium light under normal conditions, the thickening of the stratum of air seemed a more suitable expedient for the direct demonstration of the influence of the air upon the photographic efficacy of the most refrangible rays than previously. I employed for this purpose the same experimental arrangement which I had used in taking the zinc spectrum. The track of the rays in the air up to the photographic plate measured consequently again 17 mètres.

Not a single exposure now left an impression upon the plate, not even when I exposed for an hour and a half with very energetic sparks. The thickening of the stratum of air had therefore caused all the light-rays, which in the former case had left an impression, to become enfeebled on their passage to the plate to complete inefficiency. Thus I had at last obtained experimentally the confirmation of my supposition on the aërial resistance in the most refrangible ultra-violet, and at the same time the certainty that if with the resources of the present day a further advance is feasible, this can be effected only after sufficient diminution of the resistance of the air. No apparatus in my possession could be adapted to this condition. The continuance of the experiment was therefore effected chiefly with newly-acquired instruments, mentioned under "Cadmium," the arrangement of which had been brought into accord with the experience collected in photographing the most refrangible rays.

(To be continued.)

## ON THE DETERMINATION OF VANADIC ACID.*

(Continued from p. 90).

In the analysis of the vanadio-tungstates the author proceeded as follows in accordance with the results of the above investigations.

The determination of the vanadic acid was effected by the process last mentioned. The very dilute solution of the salt was strongly acidified with phosphoric and sulphuric acid, the vanadic acid was reduced with sulphurous acid, the excess of the latter expelled by boiling in a current of carbonic acid, and the vanadic acid then determined by titration with permanganate, observing the prescribed precautions.

The tungstic acid was determined indirectly, the author finding the joint weight of vanadic and tungstic acid, and then determining the latter as difference.

The vanadic and tungstic acid were precipitated with mercuric nitrate in a moderately dilute solution, as neutral as possible, and the liquid was then mixed with a few drops of ammonia until the reaction was distinctly alkaline. The precipitate was filtered off and washed with a very dilute solution of mercurous nitrate. After acidulation with sulphuric acid, the excess of mercury was precipitated by sulphuretted hydrogen, or by the mere addition of hydrochloric acid, and the precipitate was filtered off. The two mercurial precipitates were dried, and after the most careful combustion of the filters ignited in a porcelain crucible (first gently and then very strongly), and weighed. Before the check weighings the precipitate is again ignited in an atmosphere of ammonium nitrate in order to oxidise any vanadyl which may have been formed. Both precipitates were ignited together, because it was found that in the first precipitation the acids were not entirely separated, and that in general a portion is precipitated along with the mercury sulphide or chloride.

Occasionally a little vanadic acid has been still detected in the filtrate of the second mercurial precipitation. Such traces were then determined by titration with permanganate.

The author proceeded in the manner described in the analysis of the alkali and the barium salts of the vanadio-tungstic acid. For the determination of the barium a solution of potassium sulphate was added to the boiling solution of the salts in order to precipitate the barium sulphate. An addition of sulphuric acid would cause a separation of tungstic acid. Silver-vanadio-tungstate was melted with sodium-potassium carbonate for the determination of the vanadic acid, and the titration of the vanadic acid was undertaken in the usual manner in the aqueous solution of the melt. For determining the sum of both acids the salt was entered in a boiling solution of sodium nitrate, with which it is transformed into silver nitrate and sodium-vanadio-tungstate. The silver was then precipitated by a calculated quantity of solution of sodium chloride, and the sum of both acids was determined in the filtrate in the manner described above.

C. Friedheim (*Berichte Deutsch. Chem. Gesellschaft*, xxiii., p. 353) considers the determination of vanadic acid along with tungstic acid, by titration with permanganate, uncertain, as the recognition of the final reaction is attended with too great difficulties. He recommends the following method for the direct determination of both acids.

To the concentrated solution of the alkaline vanadio-tungstate he adds, in a roomy porcelain capsule placed upon a boiling water-bath, a concentrated solution of mercurous nitrate as neutral as possible, until the precipitate settles readily, and digests then with an excess of freshly-precipitated mercuric oxide for about twenty minutes, in order to neutralise the free acid. When the solution is cold, the precipitate—a mixture of the mercury salts of both acids with an excess of mercuric oxide—is filtered through a plain filter, washed with water (to which a few drops of mercurous nitrate have been added), which is effected in a short time, as the precipitate filters very readily. It is then rinsed back from the filter into the capsule, and the liquid is evaporated to the consistence of a paste. When cold it is treated, with careful stirring, with an excess of the most concentrated hydrochloric acid, covered with a watch-glass, and heated for five minutes on the boiling water-bath. Thus all the vanadium (as vanadyl chloride), almost all the tungstic acid, and the main quantity of the mercury pass into solution, as the bulk of the mercurous chloride passes into mercuric chloride in consequence of the generation of chlorine due to the action of hydrochloric acid upon the vanadic acid. To the blue solution obtained there is now added much water, by which the dissolved tungstic acid is precipitated almost quantitatively, whilst vanadium and mercury remain in solution. This solubility of the freshly-precipitated mercurous tungstate in fuming hydrochloric acid depends probably on the circumstance that, in contact with hydrochloric acid, tungstic acid behaves like a base. The author has not completed his examination of such solutions. If recently precipitated tungstic hydrate is boiled with fuming hydrochloric acid, it is likewise partially dissolved and can be re-precipitated by water. In the analysis of tungstates we must avoid mixing the acid when once separated with much hydrochloric acid, as it is often done to prevent it from running through the filter. The solution is preferably acidified with dilute sulphuric acid. The remnant of the precipitate left upon the filter is dissolved in hot sulphuric acid of sp. gr. 1·12, and the solution transferred to the capsule. After standing for twenty-four hours,

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* *Zeitschrift fur Analytische Chemie.*

during which time a little more tungstic acid is deposited, the precipitate is filtered off, washed with water, very faintly acidulated with hydrochloric acid, the residue adhering to the capsule is brought into a weighed porcelain crucible by means of a little ammonia, the contents of the crucible are evaporated to dryness; the filter, whilst still moist—if previously dried it is readily corroded—is placed in the crucible, dried in the air-bath at 120°, and ignited under the draught-hood, when pure yellow tungstic acid is obtained.

From the filtrate, after heating to 80°, the mercury is precipitated as sulphide by the prolonged introduction of sulphuretted hydrogen until the precipitate is completely deposited; the filtrate, containing vanadyl chloride, is evaporated to dryness on the water-bath, oxidised with concentrated nitric acid on the water-bath whilst covered with a watch-glass, again evaporated—repeating the operation at least twice,—and the brown hydrated vanadic acid is dissolved in water with the addition of a few drops of nitric acid.

(To be continued).

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## NOTES ON THE MICRO-CHEMICAL ANALYSIS OF ROCK-MAKING MINERALS.[*]

By Lieut.-General C. A. McMAHON, F.G.S.

(Concluded from p. 93).

### *Chromium.*

1. For the following test the chromium salt should be converted into an alkaline chromate by ignition with potassium nitrate and an alkaline carbonate. Dissolve the resulting chromate in water, and then neutralise the alkaline solution with acetic acid. Add a drop or two of a solution of nitrate of silver. The liquid turns blood-red. On spontaneous evaporation microscopic crystals of chromate of silver are deposited ($Ag_2CrO_4$). Sometimes these crystals are in very minute and short rods, and remind one of a clotted mass of some species of microbe; at other times they are of larger size and more irregular shape. They are then seen to be of blood-red colour in transmitted light, and to be transparent or translucent. In any case they require a ⅕ inch objective and the second eye-piece. As the chromate of silver is insoluble in water, all trace of the chromate of potash can be removed by washing. The residue dissolves readily on the addition of a few drops of ammonia to the slide, and on evaporation thin, branching, moss- or lichen-like clumps and tufts of $Ag_2CrO_4+4NH_3$ are deposited. These tufts are opaque to translucent, the latter being of blood-red colour in transmitted light. Powerful absorption with a single nicol (blood-red to nearly black), but between crossed nicols the double refraction is so feeble as to be nearly *nil*. In reflected light the crystals have a brilliant metallic lustre. These crystals are said (Haushofer, quoted by Klement and Renard, p. 44) to occur in elongated rhombic plates, but I have not obtained any that exhibit a definite crystallographic form.

2. To the dichromate add a drop or two of barium chloride. On evaporation the chromate of barium ($BaCrO_4$) will be found on the slide. This is insoluble in water, and is of yellowish-white colour and of granular texture. If the solution was strong the deposit will be opaque and dotted over with the cubic crystals of potassium chloride. If very dilute the barium chromate commonly yields skeleton crystals in the form of four-armed crosses. The arms of these crosses are varied and irregular in shape, but they all more or less resemble the fronds of a fern with transverse lobes. They require 1-5th inch objective, and have only a feeble action on polarised light.

### *Cæsium* (Cs).

Stannic chloride[*] gives with $Cs_2SO_4$ (orthorhombic system) a multitude of micro-crystals belonging to the cubic system (principally octahedrons) and star-shaped skeleton crystals, shaped like negative ice crystals, but consisting usually of three (occasionally four) rays.

Cæsium chloride gives with the above reagent small octahedrons and colourless crystals of the cubic system. The latter usually predominate. Cæsium chloride itself crystallises in the cubic system ($Cs_2SO_4$ is therefore to be preferred), but its habit is different from $Cs_2SnCl_6$. I have always found cæsium chloride crystallise in cubes like common salt.

The bichloride of platinum gives with the salts of $NH_3$, K, Cs, and Rb crystals similar in shape to those of $Cs_2SnCl_6$.

### *Iron* (Fe).

The ferro- and ferri-cyanides of potassium give such delicate and characteristic reactions that hardly any other tests are required to detect the presence of iron. Basic sulphates, about which little seems to be known from a microscopic point of view, are numerous, and they form on the application of heat or on a solution being allowed to oxidise in the air; and this renders the determination of iron with the aid of the microscope very difficult. Of microscopic tests the following may be mentioned:—

1. With oxalic acid, ferrous sulphate gives greenish-yellow crystals of ferrous oxalate ($FeC_2O_4+2H_2O$, solution 1 in 3800). They are of microscopic size, belong to the orthorhombic system, and have their major axis of elasticity at right angles to *c*. They are ordinarily rectangular in shape, but are sometimes prisms with six sides terminated by domes. They polarise rather brilliantly.

2. With ferrous sulphate, ammonia throws down a whitish precipitate, which at first turns green and ultimately a dull red colour. When dried on the glass slide it closely resembles a drop of dull red sealing-wax on which a plain seal has been impressed. It is only translucent here and there, being in transmitted light of bright orange-red colour. With ferric sulphate, ammonia throws down at once a foxy-red precipitate, which forms on evaporation an amorphous translucent glass of much brighter red than that formed by $FeSO_4$.

3. When ferric sulphate is dissolved in boiling water several salts seem to be formed. When allowed to evaporate on glass slides my specimens contained (*a*) needle-like prisms in groups radiating from an opaque amorphous centre—these seem to be No. 34, Part II.; (*b*) hexagonal scaly plates of micaceous habit—these seem to agree with No. 39, Part II.; and (*c*) spherulite rounded disks composed of radiating platy crystals resembling two open fans arranged so as to form a circle. They polarise brilliantly, and show radiating stripes of colour. Major axis ‖ to axis of quartz wedge. It is difficult to say whether these disks are No. 34 or No. 39 of Part II., or some other basic salt.

4. The ferrous sodium double salt (Part II., No. 41) on first crystallising forms an isotropic structureless glass. After standing for some little time it parts with some of its water and passes into the crystalline condition, forming masses of long prisms radiating from different centres, which polarise brilliantly. After further exposure to the air, and further loss of water, the salt gradually becomes a white opaque mass. This process, which is attended with loss of weight, takes place in a somewhat capricious manner, drops from the same solution evaporated side by side, behaving differently. Some take a short cut to the white opaque stage at once; others take as much as from six to ten days to accomplish it. The process may be stopped by mounting in Canada balsam.

5. The ferrous and the ferric sulphates treated with ammonium fluoride yield numerous small octahedra, cubes

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[*] *Mineralogical Magazine*, vol. x., No. 46, p. 79.

[*] $SnCl_4+3H_2O$ (in needles); $SnCl_4+5H_2O$ (opaque acute prisms); $SnCl_4+8H_2O$ (large transparent crystals). These hydrates all crystallise in the monoclinic system.

and other forms of the cubic system, the octahedra being by far the most numerous. Interesting cases of penetration twinning frequently occur.

### *Potassium* (K).

A very delicate test is the reaction with the bichloride of platinum ($PtCl_4$). It is absolutely indispensable that this reagent should be pure, and that its purity should be tested by evaporation on a glass slide and microscopic examination before it is used. The bichloride commonly sold contains potash, and yields crystals of chloroplatinate of potash, described below. The pure bichloride (that is to say, the purest I have been able to obtain) crystallises in long slender prisms like blades of grass. Extinction takes place nearly parallel to the length of the blade. Major axis parallel to *e*. The blades polarise brilliantly, usually in the blue and pink of 2nd order. The reagent must not be kept in glass bottles. I use a gutta-percha one. If a drop or two of this reagent be added to a few drops of the sulphate of potassium (or to a neutral or feebly acid solution of any other K-salt) yellow crystals of chloroplatinate of potash ($K_2PtCl_6$, solution 1 in 100) are formed. These are either octahedrons or combinations of the octahedron and dodecahedron, or some other form of the cubic system. The complex forms, however, almost always exhibit a six-sided face (a triangle with the corners cut off) of deep orange-yellow colour; the other faces of the crystal at various angles to the plane of the glass slide, owing to the high refraction of the mineral, remain dark in transmitted light. Sometimes skeleton crystals in trefoil form, or with four arms arranged as a cross, are formed.

An excess of free $H_2SO_4$ is unfavourable to this reaction.

The salts of ammonium, cæsium, and rubidium give, with the bichloride of platinum, crystals belonging to the cubic system similar in shape to those of $K_2PtCl_6$.

### *Lithium.*

1. Phosphate of soda produces a precipitate of phosphate of lithium, $Li_3PO_4+H_2O$ (solution 1 in 2500), which forms in dagger-shaped crystals (two short transverse arms representing the hilt), or in star-shaped crystals composed of four or five rays. These crystals are interspersed among numerous globulites, which give a dark cross between crossed nicols. Most of these globulites are divided into approximately two halves; and when resolved between crossed nicols, in parallel light, the cross opens up into two hyperbolic branches like axial sections of some biaxial crystals in converging polarised light. The curvature is greatest when the axis of the hyperbola is at right angles to the dividing line. In elongated individuals the result between crossed nicols is an elongated cross with two transverse arms, one on either side of the dividing line. These elongated twins are very suggestive of the multiplication of organic cells by fission. Indeed the resemblance is so close that one may readily obtain on the same slide illustrations of this supposed fission at every stage. The optical phenomena noted above are very curious, but, pending the completion of some investigations which I am carrying on, I think it better to postpone any attempt to explain them.

The crystals of lithium phosphate possess strong refraction, which shows itself in the dark boundaries of the globulites and in the strongly wrinkled surface of the crystals. The latter have straight extinction. The addition of acetic acid increases the number of globulites.

2. With the reagents mentioned below (see Magnesium, No. 2) crystals isomorphous with those of struvite are obtained. They also exhibit similar optical properties. A little warmth assists the reaction, and the phosphate of soda should be added in crystalline form. Manganese salts also yield similar results with these reagents.

### *Magnesium.*

1. With ammonia the sulphate yields a gelatinous precipitate which on spontaneous evaporation forms a colourless mass with a silky gloss on it. This is the monoclinic double salt $MgSO_4(NH_4)_2SO_4+6H_2O$ (see Part II.). Prepared on a glass slide this salt usually appears in crystals arranged like the shaft and web of a bird's feather. Mounting in Canada balsam appears to decompose the double salt. In every instance in which I have tried the experiment the monoclinic crystals of the double salt have broken up into needle-shaped orthorhombic prisms, presenting the appearance and optical properties of $MgSO_4+7H_2O$.

2. Add a *little* ammonium chloride (cubic) to a dilute solution of $MgSO_4$ (orthorhombic) in water. Place a few drops of this mixture on a glass slide. Place a drop of an aqueous solution of sodium phosphate (monoclinic) on the slide near it, and to the latter add one or two drops of ammonia. Then join the two drops. On evaporation struvite crystals will be found on the glass slide. As hemimorphism is common the shapes of the crystals are varied. The struvite crystals, $Mg(NH_4)PO_4+6H_2O$ (solution 1 in 15,000), belong to the orthorhombic system. They polarise brilliantly in the colours of the 1st and 2nd order. Major axis *R.L.* to *e*.

Most writers recommend the gentle warming of the drops prior to mixing, but I have not found it necessary. Behrens adds the phosphate of soda solid. This may be useful in some cases. The reaction requires a little practice.

Crystals similar in shape and optical properties are also produced by the action of the above reagents on the sulphates of lithium and manganese.

3. On adding some drops of the aqueous solution of potassium antimonate to the aqueous solution of $MgSO_4$ (the proportion of the latter to the antimonate should not be too great), numerous microscopic crystals of the acid pyro-antimonate of magnesia ($MgH_2Sb_2O_7+9H_2O$) are formed on the slide. These occur, for the most part, in six-sided disks lying on their basal planes, but also, not unfrequently, on one of the sides of the hexagonal prism. They also occur in cube-like prisms (sometimes slightly elongated in one direction), and in the form of little flowers, like primroses, with four (occasionally five) uniform petals. The hexagonal disks sometimes pass into globulites, and the latter are doubtless the immature form of the former. Penetration twins are not uncommon, and their forms are very varied. Double refraction is not strong, and sometimes it is *nil*. Fock refers the crystals of pyro-antimonate of magnesia to the hexagonal system

### *Manganese.*

The blowpipe and ordinary chemical tests are the most reliable for the detection of manganese.

1. Manganous sulphate (or other manganous neutral or feebly acid salt) treated with oxalic acid yields crystals of oxalate of manganese ($MnC_2O_4+3H_2O$) in radiating groups of elongated prisms with straight extinction; but as oxalic itself forms similar prisms, and groups of prisms with straight extinction,* this reaction is not recommended.

2. Ammonia produces a white precipitate, which on exposure to the air becomes of dark brown colour (chloride of ammonium prevents this precipitation). On allowing this to evaporate spontaneously on a glass slide, the crust formed is partly transparent and partly opaque. Under the microscope in transmitted light the crust becomes a very beautiful object, and is seen to be made up of fern-like fronds arranged in groups on a rich yellow-brown background. The transparent portions (sometimes the fronds are transparent, sometimes opaque) extinguish in a direction oblique to the stems of the fern-like forms.

3. With phosphate of soda $MnSO_4$ gives the same results as $Li_2SO$ and $MgSO_4$. For details see Mg, Part III., No. 2.

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* Oxalic acid is said to crystallise in the monoclinic system, but the prisms obtained on a glass slide have straight extinction. Double refraction very high. Major axis || to *e*.

### *Sodium* (Na).

The blowpipe and flame reactions are principally to be relied on for the detection of soda. Szabo's well-known method is a most useful one. The following is the process for microscopic testing which I follow. It is a good, but a somewhat troublesome, method.

1. Reduce the mineral to a fine powder in an agate mortar; ignite in platinum crucible; re-grind in mortar; ignite; add hydrofluoric acid and stir; heat gently for some time in platinum dish or crucible (agitating the liquid from time to time and adding more HF aq. if necessary) until the powder, or as much of it as is soluble in HF aq., is dissolved; cool, add water, and then heat again. This operation converts the soda and silica present into sodium fluo-silicate ($Na_2SiF_6$). Should the mineral operated on not contain silica, pure silica must be added. A glass slide must now be prepared by giving the central portion of it a thin coating of hardened Canada balsam. A few drops of the liquid are then removed by means of a platinum spoon (all the platinum employed must be pure from all surface trace of soda), and transferred to the prepared glass slide. If the liquid does not completely evaporate in forty-eight hours, the surplus can be removed by bringing a strip of filter-paper into contact with the outer edge of the drop. When this has been done the crystals left on the slide can be mounted in the usual way.

The most characteristic crystals of sodium fluo-silicate are six-sided prisms; sometimes short and terminated with rather flat pyramids (in which case they much resemble micro-crystals of quartz); sometimes comparatively long and terminated at both ends by flat basal planes. Penetration twins are not uncommon, and other forms also occur. Before mounting, the crystals sometimes lie with the apex of the flat terminal pyramid turned towards the eye of the observer. In the process of mounting they get turned over on their sides. Straight extinction. Major axis parallel to length of prism. Double refraction—white of the 1st order.

Crystals of fluo-silicate of soda are isomorphous with those of the fluo-titanate of soda.

### *Rubidium.*

1. The reaction of the salts of rubidium with platinum bichloride is the same as that of the salts of potassium, cæsium, and ammonium. See Potassium.

2. For reaction with fluoride of titanium see Titanium, No. 2, Part III.

### *Silica.*

The reaction for silica is the same as that for sodium (see *ante*). If the mineral to be tested does not contain soda, some soda must be added. Crystals of fluo-silicate of soda are isomorphous with those of fluo-titanate of soda.

### *Strontium.*

Strontium sulphate dissolves in hot concentrated $H_2SO_4$ like $BaSO_4$ (see *ante*). On cooling, embryo crystals are deposited, the lowest form of which is the micro-globulite. More advanced forms present themselves in the shape of disks, oval crystals, and acicular prisms (often forked), which sometimes arrange themselves in rosettes. The prisms and almond-shaped bodies occasionally develop radiating tufts at one or both ends. The most developed is the arrangement of almond-shaped bodies in the form of a short cross with oval arms, which gradually grows, by the filling up of the re-entering angles, into a four-sided tabular crystal. Not unfrequently we get either a combination of lenticular crystals or two disks at right angles to each other. The suppression of one half of one of the disks produces a hat-like form, which is not uncommon. In all these crystals the unit is clearly a globulite. Even the most advanced forms (the four-sided tabular crystals) may sometimes be distinctly seen to be built up of globulites. The double refraction is feeble, showing only the grey-white of the 1st order. Major axis parallel to *e* in oval disks. Straight extinction, viz., parallel to *e* in oval disks. In the cross-like forms extinction is parallel and at *R.L.* to each arm. The more gradual the cooling the more the cross-like forms abound. After mounting in balsam I have obtained comparatively large crystals of celestine (orthorhombic).

Klement and Renard state on the authority of Haushofer that a mixture of equal parts of the sulphates of Sr and Ba dissolved in hot concentrated $H_2SO_4$ gives on cooling crystals in the form of $SrSO_4$ only. Behrens says the same. My experiments do not confirm this. I have under the above circumstances obtained typical crystals of $BaSO_4$.

### *Titanium.*

1. Titanium dioxide dissolved in hydrofluoric acid* gives with the salts of potassium monoclinic crystals of fluotitanate of potassium ($K_2TiFl_6+H_2O$) in rectangular crystals, rhombs, and elongated six-sided prisms. The truncation of the corners of the former give six- and eight-sided outlines. Polarisation feeble. The best results are obtained by placing a crystal of the K-salt in contact with the acid solution. Crystals of fluoride of potassium cannot be mistaken for those of the fluotitanate, as the extinction of the former is straight and the latter decidedly oblique.

2. Strong solutions of rubidium chloride (cubic) and cæsium chloride (cubic) both give similar reactions.

3. The fluotitanate of sodium, $Na_2TiF_6$ (obtained by melting the substance to be analysed in a bead of sodium fluoride, treating with cold water first, and afterwards with hydrofluoric acid, and crystallising on a glass slide), is isomorphous with sodium fluosilicate (see Sodium, *ante*). This reaction, therefore, is of no use when silica is present.

### *Zirconium.*

1. Two or three drops of an aqueous solution of potassium binoxalate added to a solution of zirconium sulphate on a glass slide yield, on evaporation, crystals probably tetragonal (Behrens); they are in: (*a*) rectangular and six-sided prisms, principally the former, lying apparently on their basal plane with the apex of a pyramid turned towards the eye of the observer; (*b*) crystals showing a six-sided face parallel to the plane of the glass slide and bounded by faces that remain black in transmitted light. (*a*) Remain dark between crossed nicols; (*b*) the central portion polarises and exhibits a limpid gentian blue of very beautiful tone; at the margin of the drop, where the crystals are massive, the blue passes through violet into red. None of the above crystals will bear mounting in Canada balsam.

2. Zircon (and other varieties of the silicate of zirconium) is decomposed by fusion† with about five times its weight of pure anhydrous sodium carbonate. A little hydrous sodium carbonate (pure) should be added when fusion is nearly complete. After fusion treat the mass with cold water for the removal of soluble silica; dissolve the insoluble residue with hydrochloric acid; evaporate to dryness; dissolve in water acidulated with hydrochloric acid; the solution contains nearly pure zirconium chloride. Oxalic acid throws down zirconium oxalate. The crystals I have obtained in this way appear, like those described under No. 1, to belong to the tetragonal system. They present rectangular outlines with pyramids pointing to the eye of the observer truncated by a plane, the outline of which is a rhomb, the diagonals of which bisect the faces of the rectangle. Two of the edges of the pyramids are sometimes truncated towards their apex by planes which are apparently the pyramids of the 2nd order, and these planes also truncate the acute angles of

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* When HF aq., or a fluoride, is evaporated on a glass slide, the glass must be protected by a thin coat of hardened Canada balsam, as otherwise Ca, K, and other bases would be extracted from the glass.

† Behrens recommends fusion with sodium fluoride and evaporating down with sulphuric acid.

the rhomb producing a six-sided outline. The rhomb alluded to polarises in the whitish yellow of the 1st order. Major axis parallel to a line bisecting the acute angles of the terminal rhomb. Extinction parallel to the sides of the rectangle.

# THE SPECIFIC HEATS OF THE METALS.*

By JOS. W. RICHARDS, Ph.D.,
Instructor in Metallurgy, &c., in Lehigh University.

(Concluded from p. 94.)

### *Platinum.*

Dr. Irvine found 0·03, and Dulong and Petit 0·0314 by the method of cooling.

Dulong and Petit found 0·0335 (0—100°) and 0·0355 0—300°), which lead to the formula—

$$Sm = 0{\cdot}0325 + 0{\cdot}00001\,t.$$

Pouillet made a careful study of platinum in 1836, using the air thermometer up to 1200°. The data which he gives lead to the formulæ—

$$Sm = 0{\cdot}03308 + 0{\cdot}0000042\,t$$
$$S\ \ = 0{\cdot}03308 + 0{\cdot}0000084\,t.$$

Regnault found 0·03243 (12—99°).

Byström obtained rather anomalous results. He found that up to 250° the rate of increase was uniform, according to the formulæ—

$$S\ \ = 0{\cdot}032386 + 0{\cdot}00000094\,t + 0{\cdot}000000188\,t^2$$
$$Sm = 0{\cdot}032386 + 0{\cdot}00000047\,t + 0{\cdot}0000000627\,t^2$$

Above 250° Byström observed a very sudden rise, which no other observer has noted. The formula would give the true specific heat at 300°, 0·034360, while Byström records 0·034750, a sudden rise of 1·2 per cent above the curve which fits all his lower results.

Kopp obtained results varying from 0·0316 to 0·335 (15—60°), so that his observations are of no interest in comparisons of accurate data.

Weinhold also investigated platinum, but his results vary so greatly among themselves as to be worthless.

Violle has made a most careful study of platinum up to 1200°. He remarks that Pouillet's observations were in error chiefly because he used a platinum bulb for his air thermometer, which gives erroneous results because of transfusion of gases through the platinum at high temperatures. Violle used a porcelain bulb, and all the precautions possible to take in such experiments. Since these determinations and formulæ are so greatly relied on in using platinum as a pyrometer, I have considered it important that Violle's results should be thoroughly understood. The diagram of Violle's results shows the particular values found by him for the mean specific heat to zero, and their proximity to the line which he chooses as best representing his results. The greatest difference between his experiments was about 1·1 per cent at any given temperature, the greatest deviation from the assumed mean line 0·8 per cent.

$$Sm = 0{\cdot}0317 + 0{\cdot}000006\,t.$$

Violle found by direct experiment Sm (0—100°) 0·0323, which would become 0·0324 for Regnault's range of temperatures, results practically identical. We must regard Violle's results as being altogether the best we possess for platinum.

*Latent Heat of Fusion.*—Violle made five determinations of the heat in solid platinum as near to its melting-point as possible, the mean value obtained being 75·21 calories to zero. (By the formula this would indicate a maximum point of fusion of 1775°). Four experiments were made on the heat in molten metal at its setting-point, the mean value obtained being 102·39 calories to 0°. From these data the latent heat of fusion is 27·18 calories.

### *Potassium.*

Regnault found 0·1660 between −78° and +10°.

### *Rhodium.*

A specimen containing iridium gave Regnault 0·0553 (12—98°); another purer specimen 0·0580.

### *Ruthenium.*

Bunsen found 0·0611 (0—100°).

### *Silver.*

Wilcke gave 0·082; Dalton, 0·08.

Dulong and Petit found 0·0557 (0—100°) and 0·0611 0—300°), which would give the formula of two terms.

$$Sm = 0{\cdot}0530 + 0{\cdot}000027\,t.$$

Regnault obtained 0·05701 (14—99°), almost 2 per cent higher than given by the above formula.

Byström investigated up to 300° and gives his results calculated for the true specific heats at every 50° up to 300°. His figures are represented by the equations—

$$S\ \ = 0{\cdot}05698 + 0{\cdot}0000023\,t + 0{\cdot}000000032\,t^2$$
$$Sm = 0{\cdot}05698 + 0{\cdot}00000115\,t + 0{\cdot}0000000107\,t^2.$$

This equation would give for Regnault's temperatures 0·05725, about identical with Regnault's value.

Kopp obtained values varying from 0·0552 to 0·0574; mean, 0·0560 (15—65°).

Bunsen obtained 0·0559 (0—100°), a value almost identical with Dulong and Petit's.

Pionchon investigated up to 1020°. He found up to the melting-point a regular formula of three terms, viz.,—

$$Sm = 0{\cdot}05758 + 0{\cdot}0000044\,t + 0{\cdot}000000006\,t^2.$$

This equation gives for Regnault's range of temperature 0·05815, which is 2 per cent above his value. In the molten state, Pionchon found the following formula for the mean specific heat to zero:—

$$Sm = 0{\cdot}0748 + \frac{17{\cdot}20}{t}$$

the true specific heat in this condition being constantly 0·0748. The formula for the solid state would give its true specific heat at the melting-point as 0·075; we thus have another example of the specific heat in the solid state approaching equality to that in the liquid state as the melting-point is approached.

Naccari's experiments up to 300° led to the following formulæ:—

$$S\ \ = 0{\cdot}05449 + 0{\cdot}0000214\,t$$
$$Sm = 0{\cdot}05449 + 0{\cdot}0000107\,t$$

The latter, evaluated for Regnault's temperatures, gives 0·0557, which is almost identical with Dulong and Petit's value.

Le Verrier claims that the specific heat is constant up to 260°, then changes suddenly and is again constant up to 660°, then changes again and is constant to the melting-point. He gives between 0° and 260°, 0·0565; between 260° and 660°, 0·075; between 660° and 900°, 0·066. As no other observer has observed any such sudden changes, it is probable that Le Verrier is mistaken in his results. Le Verrier states that silver contains 62 calories of heat towards 930°, a little before the fusion. Pionchon places the fusing-point at 907°, and gives 60·32 calories as the amount of heat in the metal at this temperature.

It is difficult to decide just where the truth lies in this case of the specific heat of silver. If it were allowable to do so, an average of all the results at ordinary temperatures would come close to Regnault's value. But, since Pionchon made no experiments below 400°, I should be disposed to place less reliance on his values for temperatures from 0° to 100°. I would suggest for use below 400°, a formula based on the mean of Regnault's and

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* A Lecture delivered before the Franklin Institute, Jan. 30, 1893.

Bunsen's observations at 0° to 100° and on Pionchon's results at 0° to 400. Such a formula would be—

$$S = 0{\cdot}0555 + 0{\cdot}00001886\, t$$
$$Sm = 0{\cdot}0555 + 0{\cdot}00000943\, t$$

This gives for Bunsen's range 0·05644; for Regnault's range, 0·0566; being in each case about 1 per cent from their figures. At 220°, the point where it will be seen from the diagram that the lines of Byström and Naccari meet, at the value for S of 0·0590, the above formulæ gives 0·0596. At 400° the line joins in with Pionchon's curve, and above 400° Pionchon's formula may be assumed as probably accurate.

*Latent Heat of Fusion.*—Person determined this by the method of cooling to be 21·07 calories. Pionchon's formula for solid silver evaluated for the melting-point gives 60·32, and his formula for liquid silver evaluated for that temperature gives 85·04; the difference between these would therefore be the latent heat of fusion, or 24·72 calories. Pionchon's number is probably the nearest right.

### *Sodium.*

Regnault obtained 0·293 (38° to +10°).

### *Thallium.*

Regnault obtained 0·0335 (18—98°).

### *Thorium.*

Nilson obtained 0·0276 (0—100°).

### *Tin.*

Crawford found 0·0704; Wilcke, 0·06; and Kirwan, 0·068. Dalton obtained 0·07 by the method of cooling.

Dulong and Petit obtained 0·0514 by the method of cooling.

Regnault found for impure English tin 0·05695 (16—97°), and for pure Banca tin 0·05623 (14—99°).

Bède obtaided results up to 213°, from which he deduced the formula—

$$Sm = 0{\cdot}0500 + 0{\cdot}000044\, t$$

This evaluated for Regnault's temperatures gives 0·0550, over 2 per cent lower.

Kopp obtained results varying between 0·0493 and 0·0553; mean, 0·0531 (15—65°)—a result of very little value. A second set of experiments gave him results between 0·0543 and 0·0573; mean, 0·0565. The mean of the two sets of experiments is 0·0548; but the highest and lowest values he obtained were 16 per cent apart!

Person found the specific heat of molten tin to be 0·0637 (250—340°).

Bunsen found for *allotropic* tin 0·0545 (0—100°), and for cast tin 0·0559 (0—100°).

Pionchon found for molten tin up to 1000° the formula—

$$Sm\ (\text{to } 0°) = 0{\cdot}0612931 - 0{\cdot}0000104741\, t + 0{\cdot}0000000103448\, t^2 + \frac{14{\cdot}375}{t}$$

The writer has determined for Banca tin between 15° and 99°, 0·0566—a value 0·7 per cent above Regnault's.

*Latent Heat of Fusion.*—Dr. Irvine, Sen., working under Dr. Black, found that the latent heat would raise the temperature of solid tin 500° F. (at what temperature not stated). Dr. Irvine, Jun., found in a similar way 507°, the mean between 495° and 520°. In reaching these results, the heat in molten tin at its setting-point was first found. This was divided by the ordinary specific heat of tin, and the melting-point subtracted. This would be equivalent to assuming that the heat in solid tin at its melting-point is the product of that temperature into the ordinary specific heat. Since we do not know what value Irvine assumed for the latter we cannot correct his figures. If he used Crawford's value, 0·0704, his result would represent about 18·3 calories; if he had used 0·0570, his result would have been 16 calories.

Rudberg worked by the method of cooling, and assuming that the spectfic heat of solid tin at its melting-point is 0·0586, he obtained 13·31 calories as the latent heat of fusion. If we assume that the specific heat at this temperature is the same as Person found for molten tin (0·0637), Rudberg's results would become 14·46 calories.

Person found the amount of heat in molten tin at its setting-point to be 27·33 calories. Then, assuming that Regnault's value for the specific heat was applicable to the melting point, he found the heat in solid tin at its melting-point to be 232·7 × 0·05623 = 13·08 calories, which left 14·25 calories as the latent heat of fusion. Had he used the amount found by Bède in solid tin, at its melting-point, by direct experiment, he would have had—

$$27{\cdot}33 - 13{\cdot}60 = 13{\cdot}73$$

calories as the latent heat.

Pionchon's formula for liquid tin evaluated for the melting-point gives 28·20 calories. Subtracting Bède's value for the heat in solid tin leaves 14·60 calories as the latent heat.

Direct experiment, by pouring liquid tin just at its melting point into water, has given the writer 28·16 calories. This, less 13·60, would leave 14·56 calories as the latent heat of fusion. The close agreement of this result with Pionchon's is worthy of notice, especially since the heat in the molten tin was determined by two entirely different methods of procedure.

### *Titanium.*

Nilson and Petterssen determined the mean specific heat as follows:—

| | |
|---|---|
| 0° to 100° .. .. .. .. | 0·1125 |
| 0 to 211 .. .. .. .. | 0·1288 |
| 0 to 301·5 .. .. .. .. | 0·1485 |
| 0 to 404 .. .. .. .. | 0·1620 |

These would give the formula—

$$Sm = 0{\cdot}0978 + 0{\cdot}000147\, t$$

This formula fits almost exactly the first, second, and last of the above observations, but gives 0·1421 for the third. A regular curve could not be found passing through all four of those values.

### *Tungsten.*

Regnault gives 0·03636 (11—99°).

### *Uranium.*

Blümcke found 0·02811, 0·02762, 0·02813; mean, 0·0280 (0—99°). Zimmerman found on two specimens as a mean value 0·0275 and 0·2812 (0—99°).

### *Zinc.*

Wilcke found 0·102; Crawford, 0·0943; and Dalton, 0·10.

Dulong and Petit found 0·0927 (0—100°) and 0·1015 (0—300°). These results would give the formula—

$$Sm = 0{\cdot}0883 + 0{\cdot}000044\, t$$

Neumann obtained 0·0929, at ordinary temperatures, by the method of cooling.

Regnault obtained with commercial zinc 0·09985, 0·10049, 0·100003, and with chemically pure zinc 0·09555 (14—99°).

Bède deduces from his experiments the formula—

$$Sm = 0{\cdot}0865 + 0{\cdot}000044\, t$$

He observes that his metal contained a little lead.

Dulong and Petit's result is 3 per cent, and Bède's 4 per cent below Regnault's.

Kopp obtained results varying between 0·0899 and 0·0977; mean, 0·0932 (15—65°).

Bunsen obtained 0·0935 (0—100°).

Naccari deduces from his experiments up to 320° the formula—

$$S=0\cdot0907+0\cdot000044\ t$$

This gives 0·0932 for Regnault's temperatures.

Le Verrier states that from 0° to 110° the specific heat of zinc is constantly 0·096; between 110° and 140° it is very variable, there being an absorption of 0·8 calorie about 110°; that from this point to 300° the specific heat is constantly 0·105, and between 300° and 400° constantly 0·112. The total amount of heat is about 46 calories at about 410°—a trifle before fusion.

*Latent Heat of Fusion.*—Dr. Irvine, assuming the specific heat of zinc constant to the fusing-point (0·0943), found by experiment 62·5 calories in molten zinc, and subtracting the heat in solid zinc at its melting-point (388·9° × 0·0943), he obtained 62·5 − 35·7 = 26·8 calories as the latent heat. (I have transferred his Fahrenheit degrees to Centigrade).

Person obtained an average of 67·81 calories in molten zinc at its setting-point, and assuming Regnault's value for the specific heat true to the melting-point, he found the latent heat to be—

$$67\cdot81-(415\cdot3\times0\cdot09555)=67\cdot81-39\cdot68=28\cdot13$$

calories. However, we know that this latter assumption is incorrect.

Supposing we take for the mean specific heat a line which would pass through Regnault's result and be parallel to Dulong and Petit's and Bède's lines, which are parallel to each other. Such a line would be—

$$Sm=0\cdot09058+0\cdot000044\ t$$

Now, Dulong and Petit's formula would give for the heat in solid zinc at its melting-point 44·2 calories, Bède's 43·5 calories, and Naccari's 40·4 calories. The above formula gives 45·2 calories. It is noticeable that when Le Verrier gives the total heat in any metal close to its melting-point, his value is usually near to the best determinations. He says there is about 46 calories in zinc just below its melting-point. I should, therefore, take the value 45·2 given by the above equation as probably the nearest right.

Irvine's result will now become 62·5 − 45·2 = 17·3 calories. Person's results, 67·81 − 45·2 = 22·61 calories. Person's is, of course, the better determination of the two.

### *Zirconium.*

Mixter and Dana have obtained 0·0662 (0—100°) with the ice calorimeter.

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## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, June 15th, 1893.*

Dr. Armstrong, President, in the Chair.

(Continued from p. 98).

40. "*Sarcolactic Acid obtained by Fermentation of Inactive Lactic Acid.*" By Percy Frankland, F.R.S., and J. MacGregor, M.A.

The authors have submitted ordinary inactive calcium lactate to partial fermentation, and have recovered from the fermented liquid a lactic acid yielding lævorotatory salts, which was separated from the inactive acid still present by repeated crystallisation of the zinc salts, the zinc salt of the inactive acid being less soluble than that of the active acid.

The specific rotatory power of the active zinc salt was determined in several specimens and for several different concentrations, and results were obtained showing that the rotation on the whole diminishes as the concentration increases, and agrees fairly closely with those given by Wislicenus (*Annalen*, clxvii., 332).

The identity of the two salts was further established by converting some of the zinc into the calcium salt and determining the specific rotatory power of the latter; the value found ($C=5\cdot79$) was $[\alpha]_D=-5\cdot48$, that given by Wislicenus ($C=5\cdot35$) being $[\alpha]_D=-5\cdot25$.

The authors hope to render this method available for the preparation of considerable quantities of sarcolactic acid, in the same way as has already been done by one of them in the case of active glyceric acid. In the meantime it is of interest to note that, as in the case of the fermentation of calcium glycerate, the bacteria attacked by preference the dextrorotatory salt. Similarly, Linossier (*Ber.*, xxiv., 660) has shown that *Penicillium glaucum* also first destroys the dextrorotatory lactate.

41. "*Hexanitroxanilide.*" By A. G. Perkin.

It is shown that whereas di- and tetra-nitroxanilide are converted by ammonia into the corresponding nitraniline (*cf. C. S. Trans.*, 1892, 458), hexanitroxanilide not only yields trinitraniline, but also trinitrophenoxamide, $C_6H_2(NO_2)_3{\cdot}NH{\cdot}CO{\cdot}CONH_2$, a substance which crystallises from nitrobenzene in colourless glistening needles melting at 257°; this compound exhibits acid properties, forming potassium, sodium, and ammonium derivatives, *e.g.*, $C_6H_2(NO_2)_3{\cdot}NR{\cdot}C_2O_3NH_2$, which crystallises in red leaflets, exhibiting a magnificent golden lustre. When subjected to the action of a cold mixture of nitric and sulphuric acids, trinitrophenoxamide loses the elements of a molecule of ammonia, forming trinitroxanil. Hexanitroxanilide is converted into 1 : 3 : 5-trinitrobenzene by heating it with a mixture of nitric and sulphuric acids; tetranitroxalorthotoluidine in like manner yields 1 : 3 : 5-dinitrotoluene, but the isomeric para-derivative is converted into dinitrobenzoic acid.

Hexanitrocarbanilide has also been prepared by the author; like the corresponding nitroxanilide, it yields red potassium and sodium derivatives.

42. "*The Constituents of the Indian Dye-stuff Kamala* (I)." By A. G. Perkin.

A description is given of six distinct substances extracted by ether from Kamala—Rottlerin, the principal constituent, described by Anderson, in 1855 (*Journ. Chem. Soc.*, 1855, 669); isorottlerin; two resins, one of low, the other of high melting-point; a wax, which is possibly cetylic cerotate; and a yellow crystalline colouring-matter present in a minute proportion, the composition of which is yet to be determined.

*Rottlerin* is best separated from the dye-stuff by means of cold carbon bisulphide, from which it crystallises in thin salmon-coloured plates melting at 191°; its composition is represented by the empirical formula $C_{11}H_{10}O_3$ already assigned to it by Anderson, but it is undoubtedly a substance of high molecular weight. It yields a diacetyl derivative. On boiling it with alkalis an odour of benzaldehyd is apparent. When oxidised by cold nitric acid it yields two acids represented by the formulæ—

$$C_{17}H_{14}O_9 \text{ and } C_{17}H_{16}O_9,$$

while boiling nitric acid converts it into a dibasic acid of the formula $C_{13}H_{10}O_9$.

*Isorottlerin* closely resembles rottlerin in appearance, but melts at 198—199°, and is practically insoluble even in hot carbon bisulphide; moreover, no odour of benzaldehyd is apparent when it is boiled with alkali. It yields the acid of the formula $C_{13}H_{10}O_9$ on oxidation.

The resin of low melting-point resembles rottlerin, with which it is evidently closely allied in most of its properties; its composition is represented by the formula $C_{12}H_{12}O_3$; on oxidation it yields the acid of the formula $C_{13}H_{10}O_2$.

The resin of high melting-point is a light-yellow coloured substance represented by the formula $C_{13}H_{12}O_4$, and also resembles rottlerin in many of its properties, being converted into the acid of the formula $C_{13}H_{10}O_9$ when boiled with nitric acid.

43. "*A Quantitative Method of Separating Iodine from Chlorine and Bromine.*" By D. S. Macnair, Ph.D., B.Sc.

The method is based on the fact that when treated with potassium bichromate and concentrated sulphuric acid, silver iodide is completely converted into silver iodate, whereas silver chloride and bromide are converted into sulphate. Two portions of a solution containing the three halogens are precipitated with silver nitrate: the one precipitate is weighed, the other is heated with the oxidising mixture and the resulting iodate is then reduced by means of sulphurous acid, and the iodide is filtered off and weighed. The silver originally present as chloride and bromide contained in the filtrate from the iodide is precipitated and weighed as chloride. The method affords very accurate results.

*Addendum.* — Since the paper was written, at the suggestion of Dr. Armstrong I have used a Gooch crucible asbestos filter, instead of paper, and have found it advantageous both as regards speed and accuracy, as it is not necessary to use two portions of the liquid when the chlorine and bromine are to be determined; the precipitate of the mixed haloids may be dried at 120°, weighed, and then treated with sulphuric acid and potassium bichromate as usual, along with the asbestos previously used in filtering. When the oxidation is finished, the solution is diluted and sulphurous acid is added at once, *without* previously filtering off the asbestos, which is collected along with the silver iodide. The weight of the asbestos used in the first filtration is necessarily deducted from that of the silver iodide. It is evident that this asbestos might be removed by filtering before adding sulphurous acid; but I do not recommend this, as silver iodate is apt to separate out during the filtration, and unless this be *completely* re-dissolved—no easy matter—before the addition of sulphurous acid, it will escape reduction and the results will be unreliable.

44. "*Note on a form of Burette for Rapid Titration.*" By Llewellyn Garbutt, Assistant Master at Winchester College.

The following arrangement will be found extremely convenient in volumetric operations with liquids. The liquid to be used in titrating is contained in the flask F, which may have a capacity of 300 c.c., and is delivered from a pinch-cock or stop-cock C, at the bottom of the long syphon tube T. The tube D is connected by means of rubber tube to the gas burette G. The side tube B is closed by a pinch-cock, and the graduation of G begins from the bottom. The pressure tube H, which contains water, moves freely upwards, but its downward movement is arrested by the cork A, fixed stiffly to the upper end of the tube H, and normally serving as a support to it. Before beginning the titration the pinch-cock B is opened for a moment to equalise the pressure. The quantity of water in the two tubes is adjusted once for all, so that whenever the pressure is equalised the water in G falls to zero on the scale. The titration is conducted from the cock C in the usual way, and the amount delivered is read by raising H until the liquids are at the same level in both tubes. The parallel lines drawn across the supporting-board serve as a guide to the eye. The volume of the liquid delivered can then be read off from the position of the water in G. To begin a new titration, all that is necessary is to let H slide back to its normal position, and open the pinch-cock at B for a moment; the water in G at once falls accurately to zero, and the new titration can be begun. If it is desired to use several different liquids, as many flasks, furnished with syphon and connecting tubes, should be prepared and mounted ready on stands. They can then be connected in a moment with the rubber tube E.

The advantages of this arrangement are—

1. Extreme rapidity and simplicity of adjustment to zero.

2. As much as 300 c.c. of the liquid may be available for a series of titrations.

3. The same burette is used with all liquids, and always starting from zero, so the graduation is constant.

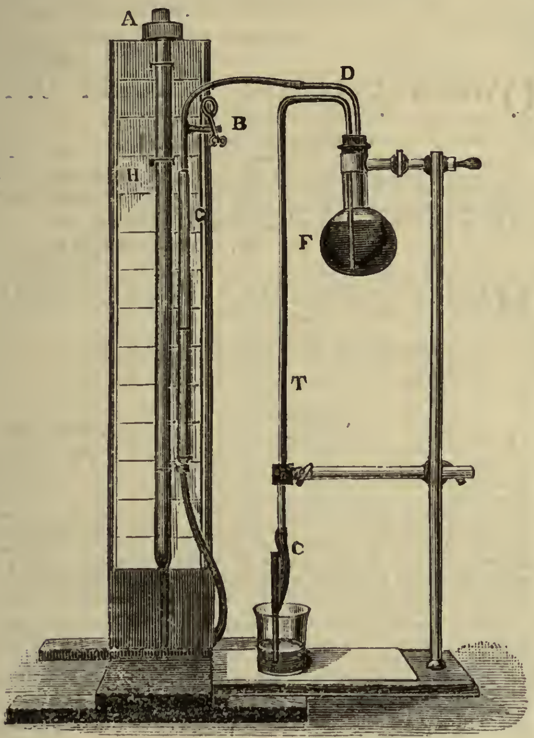
4. If the burette and pressure tube are thoroughly clean, there is little trouble from tears or imperfect meniscus, as only pure water is used in it.

The disadvantages are—

1. The titration must be conducted fairly rapidly (say within five or ten minutes), otherwise changes of tempera-

ture and pressure may appreciably affect the volume of the air.

2. The pressure cannot be *perfectly* equalised by means of the sliding tube, H. The error of reading from this cause is practically *nil* when F is full, but it might, as an extreme, amount to one-twentieth c.c. when F contains 300 c.c. of air. If it is only desired to read to one-tenth c.c. this will not matter much. For greater accuracy the flask must always be kept nearly full.



It is convenient to be able to detach H completely from the board. If the water should get out of adjustment, so that it no longer falls to zero on opening the pinch-cock at B, either a few drops of water may be added or the cork A moved a trifle along the tube H.

45. "*The Use of Sodium Peroxide as an Analytical Agent.*" By J. Clark, Ph.D.

Experiments are described showing that the sulphur and arsenic in minerals may be rendered soluble by cautiously heating the powdered substance with sodium peroxide, and that the peroxide may, in like manner, be used in estimating chromium in chrome ores and chromium alloys.

An ammoniacal solution of the peroxide may be used in separating manganese from zinc, nickel, and cobalt, a single precipitation sufficing in the case of zinc.

46. "*Stibiotantalite: a New Mineral.*" By G. A. Goyder.

The note has reference to a mineral from the alluvial tin-field at Greenbushes, Western Australia, the assay values of which varied most unaccountably. It is shown to consist, in the main, of antimony and tantalum oxides and a not inconsiderable proportion of niobic oxide; the amounts found in one sample, for example, were $Ta_2O_5$ = 51·13, $Nb_2O_5$ = 7·56, $Sb_2O_3$ = 40·23.

(To be continued.)

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 7, August 14, 1893.

**A Product of the Incomplete Oxidation of Aluminium.**—M. Pionchon.—If submitted to the action of the pointed flame of an oxyhydrogen blowpipe with a low yield of oxygen, aluminium becomes oxidised with a bright incandescence, and is converted into a substance of a blackish grey appearance, in which the proportion of the weight of oxygen to that of aluminium is close upon 0·6, and consequently very different from the value 0·888 characteristic of alumina. The product, along with free aluminium and alumina, consists of a new aluminium oxide, $Al_6O_7 = Al_2O,3Al_2O_3$. It may be a mixture or a compound.

**New Reaction of Eserine and a Green Colouring Matter Derived from the same Alkaloid.**—Sen. S. J. Ferreira da Silva.—The author announced in 1890 that eserine was the only alkaloid of the benzenic ammoniacal group which after treatment with fuming nitric acid of specific gravity 1·4 and evaporation to dryness gave a green residue along its edges. He finds that this reaction is very suitable for the identification of very small quantities of eserine. He takes a minute fragment of eserine or of one of its salts, places it in a small capsule of porcelain, and dissolves it in one or two drops of fuming nitric acid. He thus obtains a light yellow solution, which, if heated in the water-bath, turns first to a deep yellow and then to an orange. If it is evaporated to dryness whilst stirring with a glass rod, we remark in one or two minutes after complete desiccation a change of colour to a pure green. The green colouring matter thus produced is soluble in water and still more readily in concentrated alcohol. Its green solutions are not fluorescent, and yield on evaporation the green colouring matter unaltered. The aqueous solution of the green matter, if examined with the spectroscope, is characterised by two absorption bands: one, the more distinct, situate in the red between λ 670 and λ 688; the other, broader, but having less sharply-defined edges, occupies a part of the indigo and the violet, especially between λ 400 and λ 418. There is also a very faint band in the orange. The reaction shows 0·005 grm. of the alkaloid. The author proposes for the green compound the name of chloreserine.

**Preparation of Citric Acid by Synthesis.**—Charles Wehmer.—The author obtains citric acid by the fermentation of glucose set up by certain fungi, *Citromycetes pfefferianus* and *C. glaber*. Herr Wehmer states the spores of these fungi are abundant in the air, and can be obtained pure by cultivation.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 12.

**Alleged Diffusibility of Certain Gases through a Membrane of Caoutchouc.**—A. Reychler.—The facts brought forward prove that it is not necessary to ascribe to sulphurous acid, to carbonic acid, or to a mixture of both, an abnormal speed of diffusion. We must take account of the special affinity of caoutchouc for the gases present. When a membrane of caoutchouc is interposed between sulphurous acid and the free air it becomes saturated with sulphurous acid on one of its surfaces, whilst the opposite surface allows the gas to escape into the atmosphere. Air has not a great affinity for caoutchouc, whence its component gases penetrate only to a trifling extent during the absorption of the sulphurous acid.

Acrylic Anhydride (Propenoide).

Action of Acrylchloride upon Alcohols and Phenols.

Acrylamide (Propene-amide).

Certain Substituted Acrylamides.

Acrylic Nitrile, Vinyl Cyanide, and Propene Nitrile.—These five papers, by M. Moreu, on the derivatives of nitrile, will be inserted if space allows.

Influence of Certain Organic Solvents upon Rotatory Power.—Freundler.—It is necessary to eliminate benzene, chloroform, and carbon tetrachloride if it is desired to determine the laws of the rotatory power. It is still necessary to study more closely the influence of concentration in order to see in what cases we may compare the values given by acetonic or alcoholic solutions with those given by ether.

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PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that THE ELECTROLYTIC CAUSTIC AND CHLORINE TRUST, LIMITED, of 23, Queen Victoria Street, London, have applied for leave to amend the Specification of the Letters Patent No. 2296 of 1890, granted to James Charles Richardson and Trevenen James Holland, for "Improvements in the electrolytic production of caustic soda, caustic potash, and other products from their salts."
Particulars of the proposed Amendments were set forth in the Illustrated Official Journal (Patents) issued on the 23rd August, 1893.
Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the Amendment within one calendar month from the date of the said Journal.
(Signed) H. READER LACK,
Comptroller General.

The CHEMICAL DEPARTMENT of UNIVERSITY COLLEGE, LIVERPOOL, provides a four years' Course of Instruction in Chemistry. Classes in the departments of German, Mathematics, Physics, and Engineering are included in the Course. The Sheridan-Muspratt Chemical Scholarship of £50 per annum, for Students of the third year, will be offered in December, 1893. The Examination is not limited to University College Students. For particulars apply to the Registrar.

OWEN'S COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.
Prospectuses for the Session 1893—94 will be forwarded on application.
I.—DEPARTMENT OF ARTS, SCIENCE, AND LAW.
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FACULTIES OF ARTS AND SCIENCE.
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SESSION 1893—94.
The SESSION will commence on MONDAY, OCTOBER 2nd.
R. C. JEBB, Esq., Litt.D., M.P., Regius Professor of Greek in the University of Cambridge, will distribute the Prizes, and deliver an Inaugural Address at a Public Meeting in the College on Monday, October 9.
COMPLETE COURSES OF INSTRUCTION are provided for the various Examinations in Arts and Sciences, and the Preliminary Scientific (M.B.) Examination of the University of London, for Students of Civil, Mechanical, or Electrical Engineering, and for those who desire to obtain an acquaintance with some branch of Applied Science. Students may, however, attend any Class or combination of Classes.
(*There is also a Faculty of Medicine. A Syllabus containing full particulars is published by Messrs. Cornish, New St., Birmingham. Price 6d., by Post 7½d.*).
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During the Session, which commences September 25th, Classes in Organic and Inorganic Chemistry will be held on Monday, Tuesday, Thursday, and Friday Evenings under the direction of Dr. MACNAIR.
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Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at ROBERT RUMNEY'S, Ardwick Chemical Works, Manchester.

# THE CHEMICAL NEWS.

Vol. LXVII., No. 1763.

## (STUDENTS' NUMBER).

## ADDRESS TO STUDENTS.

In view of the re-commencement of study at our various colleges it is our duty to say once more a few words, not only to students, but to professors and teachers, and above all to examiners. We trust that these different bodies will bear with us, considering our motive, the advancement of Science in Britain and its Colonies. We can scarcely say that the prospects of our country take a notably high rank in the realms of research and discovery. The protest of Mr. Auberon Herbert and his associates let in a temporary light upon the question of higher education; but the attention created was but short-lived. The protest was never met, much less refuted; other less important topics engrossed the public mind, foremost among which must rank the political agitation of the present day. Hence, for all that appears on the surface, Mr. Herbert might as well never have written a word on the subject. The sad game of "setting papers" and preparing for "exams." still continues. Youths, as Mr. Huxley put it, study "not to know, but to pass." Heads of the higher grades of schools still boast, in their prospectuses, of the success of their pupils at this or the other competition, and the notorious examiner is still admired and envied. When a certain young lady surpassed the Cambridge senior wrangler at an examination the press was instant with loud voices in laudatory comment. But no one uttered the obvious truth that if Miss Fawcett had ascertained a novel fact in any of the sciences, or established a new generalisation, she would have deserved infinitely higher congratulations.

As we stand, the individual is nearly powerless. If the student seeks merely to *discover* he is elbowed aside as a failure. If the teacher aims at training his pupils to be successful in research, they will fail to pass and he will be pronounced incompetent. The utmost which he can effect is, whilst seeking to qualify his disciples for success at the examinations, to instil into their minds as much genuine truth as he can venture. But, as he values his "bread and butter," he must keep his attention mainly for passing. Indeed, his easiest way to emolument and reputation is to treat the examinational successes of his pupils as the one thing needful. He must be something more than an ordinary man if he acts differently. The examiner, again, is powerless. He must "set papers," devised, it is supposed, to test the proficiency of the pupils. He cannot take any method of guaging their intellectual resources, their accuracy of observation and of conclusion. He is simply a wheel in the great cram-mill, and he must act accordingly.

The only full help, as far as we can see, must come from the governing bodies of universities, medical schools, &c. But meantime much might be done by the press and by the public if it would, "unresting and unhasting," work against examinationism in all its phases. Mr. Auberon Herbert's protest should be followed up wherever and whenever feasible.

The student, we are aware, can here do little; nor has the teacher much more power. The examiner will not, of course, be active in a movement which would lead to his own displacement. But many less hopeful and less needed causes have been won by perseverance.

It is of course quite premature to expect any aid from the legislature. The reform which we hope for lies distinctly outside the boundaries of faction, and will therefore meet with no Parliamentary support. But opportunities may be taken of bringing the shortcomings and evil effects of the examinational system under the notice of members of either house, and inducing them to ask questions.

## UNIVERSITIES AND COLLEGES.

### UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages: — Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

### INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 16, 1894.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

#### *Examination for Honours.*

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

### B.Sc. EXAMINATION.

The B.Sc. Examination will be held October 15, 1894.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

#### *Examination for Honours.*

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

### DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

### PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

## UNIVERSITY OF OXFORD.

*Waynflete Professor of Chemistry.*—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus.*

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; the Examination Statutes, 1893; the Student's Handbook to the University; and from the professors.

## UNIVERSITY OF CAMBRIDGE.

*Professor of Chemistry.*—G. D. Liveing, M.A., F.R.S.

*Jacksonian Professor of Natural and Experimental Philosophy.*—J. Dewar, M.A., F.R.S.

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* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass *at the same time* in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B Sc. Examination.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

## UNIVERSITY OF DUBLIN.

### Trinity College.

*Professor of Chemistry.*—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

*Assistant Lecturer.*—Emil A. Werner, F.C.S., F.I.C.

*Demonstrator.*—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

*The Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

## KING'S COLLEGE.

### (Department of Engineering and Applied Science).

*Professor of Chemistry.*—J. M. Thomson, F.C.S.

*Demonstrator of Practical Chemistry.*—G. S. Johnson, F.C.S.

*Assistant Demonstrator.*—Herbert Jackson, F.C.S.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

*Second Year.*—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

*Experimental and Analytical Chemistry in the Laboratory.*—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. 0d.; per ann., £8 8s. 0d.; Practical Chemistry per term, £4 4s. 0d.; per ann., £10 10s. 0d.; Experimental and Analytical Chemistry —Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three months, £6 6s.; Six months, £11 11s.; Nine months, £5 15s.

### *Rules as to Admission of Students.*

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students: in the Academical Year 1893-94, are Tuesday, October 3, Wednesday, January 10, and Wednesday, April 11.

### Metallurgy.

*Professor.*—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

### Photography.

*Lecturer.*—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

### Evening Classes.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

## UNIVERSITY COLLEGE.

### Faculty of Science.

*Professor.*—William Ramsay, Ph.D., F.R.S.

*Assistant Professor.*—J. N. Collie, Ph.D.

*Assistants.*—James Walker, D.Sc., Ph.D., and Alexander Kellas, B.Sc.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Tuesday, October 3rd, until Wednesday, December 20th ;

Second Term, from Tuesday, January 9th, 1894, till Friday, March 16th ;

Third Term, for Lectures, from Tuesday, April 10th, till Friday, June 29th. Class Examinations begin on Monday, June 18th.

### *Junior Courses.*

First Term : Tuesday, Thursday, and Saturday, at 10, commencing October 5, 1893. Third Term : Tuesday and Thursday at 10, Friday at 4, beginning April 12th, 1894. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

### *Senior Course of Chemistry.*

First and Second Terms : Inorganic.—The Class meets four times a week : Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 4th.

Fee :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

### *Advanced Course of Chemistry.*

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

### *Organic Chemistry.*

Tuesday and Thursday, at 9, in the First Term, beginning October 5th ; Tuesday, Thursday, and Saturday, at 10, in the Second Term ; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours ; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s. ; for the Second and Third Terms, £4 14s. 6d. ; for a Term, £2 12s. 6d.

### *Practical Class.*

First and Second Terms, Tuesday and Thursday, at 11, commencing October 4th.

Fee, including cost of materials, £5 5s. ; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

### *Senior Practical Class.*

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term ; also Tuesdays and Thursdays from 11 to 12.

Fee :—(Including cost of materials) £5 5s. ; for a Second Course, £3 3s.

### *Analytical and Practical Chemistry.*

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees : for the Session, £26 5s. ; six months, £18 18s. ; three months, £10 10s. ; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s. ; six months, £11 11s. ; three months, £6 6s. ; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1893-94; also the Clothworker's Scholarship of £30.

### *Chemical Technology.*

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects :—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Methods for the Technical Chemical Analysis of Raw and Manufactured Products. Coal-tar Products and Colours. Applications of Chemistry to Engineering. Methods of Technical Chemical Analysis.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

## ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

*Professor.*—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

*Assistant Professor.*—W. P. Wynne, D.Sc., A.R.C.S.

*Demonstrators.*—H. Chapman Jones and A. E. Tutton.

*Assistants.*—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 4th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

| | Lectures. £ | Laboratory. £ |
|---|---|---|
| Chemistry | 3 | 13 |
| Physics | 5 | 12 |
| Biology with Botany | 5 | 12 |
| Geology with Mineralogy | 4 | 8 |
| Mechanics | 4 | 6 |
| Metallurgy | 2 | 13 |
| Mining | 4 | |
| Astronomical Physics | 2 | 3 |

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

*Bona fide* teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

*Summer Courses for Teachers.*—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

*Working Men's Lectures.*—Notification of these will be given in the newspapers.

## THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-second Session will commence on Monday, October 2nd, 1893. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 1 p.m. on that day.

*Officers of the School:*—Prof. Dunstan, M.A., F.R.S., F.I.C., Chemistry (Dean); Prof. Attfield, Ph D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany; Prof. Greenish, F.I.C., F.L.S., Materia Medica; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to Mr. F. W. Short, B.Sc., Secretary to the School, 17, Bloomsbury Square, London, W.C.

## UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

*Professor.*—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

*Demonstrator.*—A. W. Warrington, M.Sc. (Vic.), F.I.C

The College is open to male and female students above the age of sixteen years. The Session commences on Friday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

*Lecture Courses.*—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

*Laboratory Courses.*—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

*Fees.*—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

*Scholarships and Exhibitions* varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

## UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

*Chemistry.*—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, C. F. Archibald.

*Physics.*—Professor, Andrew Gray, M.A., F.R.S.E. Assistant Lecturer and Demonstrator, R. W. Stewart, D.Sc.

The Session opens October 3rd, 1893. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

*Matriculation Course.*—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

*Intermediate Course.* — Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

*B.Sc. Course.*—Organic Chemistry. Fee for the Session, £3 3s.

*Medical Course.*—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

*Agricultural Chemistry.*—Fee, £1 1s.

*Laboratory Courses.*—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

## UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

*Professor.*—C. M. Thompson, M.A., D.Sc., F.C.S.

*Demonstrator.*—E. P. Perman, D.Sc., F.C.S.

The Session commences October 2nd, and terminates on June 22nd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 50 lectures held during the Lent term in continuation of the Junior Course, and, together with laboratory practice and the course on Chemical Theory, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £3 3s.

A course of about 20 lectures on the Theory of Chemistry will be given during the summer term.

The Senior Course consists of some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

A course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a conjoint College Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

## UNIVERSITY COLLEGE, BRISTOL.

*Professor of Chemistry.*—Sydney Young, D.Sc., F.R.S.

*Lecturer.*—Arthur Richardson, Ph.D.

The session 1892-93 will begin on October 5th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood haveconsented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is incorporated with the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

### Day Lectures.

*Inorganic Chemistry.*

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

*Junior Course.*—Two Lectures a week will be given during the First and Second Terms.

*Senior Course.*—Three Lectures a week will be given throughout the Session.

*Organic Chemistry.*

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session.

*Practical Chemistry.—Laboratory Instruction.*

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

| | 5 Days a Week. | 4 Days a Week. | 3 Days a Week. | 2 Days a Week. | 1 Day a Week. |
|---|---|---|---|---|---|
| Per Session .. .. | 15 | 12½ | 10 | 7½ | 5 |
| „ Two Terms .. | 11 | 9 | 7½ | 5½ | 3½ |
| „ One Term .. | 7 | 6 | 4½ | 3½ | 2½ |

Students may arrange to divide their days of laboratory work into half-days.

*Photographic Chemistry.*

Special arrangements can be made with regard to instruction in this subject.

*Chemical Scholarship.*—Among others, a Chemical Scholarship of £25 is offered for competition.

### Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

## MASON SCIENCE COLLEGE, BIRMINGHAM.

*Professor.*—W. A. Tilden, D.Sc. Lond., F.R.S., F.I.C.
*Assistant Lecturers.*—W. W. J. Nicol, M.A., D.Sc. Edin., F.I.C., and Thomas Turner, Assoc.R.S.M., F.I.C.
*Demonstrator.*—Sidney Williamson, Ph.D., F.I.C.

The Session will be opened on Monday, October 2nd, 1893.

*Elementary Course.*

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

*General Course.*

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

*Advanced Course.*

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

*Laboratory Practice.*

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

| | All day. | Three hours per day. |
|---|---|---|
| One Term .. .. .. | 7 guineas .. .. | 4½ guineas. |
| Two Terms .. .. | 13 „ .. .. | 8½ „ |
| Threee Terms .. .. | 18 „ .. .. | 12 „ |

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

*Metallurgy.*

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

*Evening Classes.*

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

*Excursions.*

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

## BRADFORD TECHNICAL COLLEGE.

### Chemistry and Dyeing Department.

*Professor.*—Mr. Arthur Dufton, B.A. (Cantab.), B.Sc. (Lond.).

*Lecturer on Botany and Materia Medica.*—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 18th and terminates on July 22nd. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

## ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

### Chemical Department.

*Professor.*—Prof. E. Kinch, F.C.S., F.I.C.

*Assistants.*—Cecil C. Duncan and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

## VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

*Professor of Chemistry.*—Arthur Smithells, B.Sc. Lond., F.I.C.

*Lecturer in Organic Chemistry.*—Julius B. Cohen, Ph.D., F.I.C.

*Assistant Lecturer in Agricultural Chemistry.*—Herbert Ingle, F.I.C.

*Demonstrators.*—C. F. Baker, Ph.D., B.Sc., and A. C. Wright, B.A.

The Session begins October 10, 1892.

### *Lecture Courses.*

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

### *Laboratory Courses.*

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

*Class in Practical Chemistry*, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

*Practical Chemistry for Medical Students.*—October to end of March, at times to be arranged.

*Practical Course in Sanitary Chemistry.*—At times to be arranged.

*Practical Organic Chemistry for Medical Students.*—On Mondays, from 11 to 1, from April to July.

### *Evening Class.*

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

### *Dyeing Department.*

*Professor.*—J. J. Hummel, F.I.C.

*Lecturer and Research Assistant.*—A. G. Perkin, F.R.S.E.

*Assistant Lecturers.*—W. M. Gardner and J. B. Shaw.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

### *Leather Industries Department.*

*Lecturer.*—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

### *Agricultural Department.*

*Professor.*—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

## UNIVERSITY COLLEGE, LIVERPOOL.

*Professor.*—J. Campbell Brown, D.Sc.

*Lecturer on Organic Chemistry.*—C. A. Kohn, B.Sc., Ph.D.

*Demonstrators and Assistant Lecturers.*—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and S. B. Schryver, B.Sc., Ph.D.

*Assistant.*—H. H. Froysell.

The Session commences October 2nd.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

### *Lecture Courses.*

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

### *Practical Classes.*

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

### *Chemical Laboratory.*

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

Table of Fees.

| Per Week. | One Term, Three Months. | Three Terms, One Session. |
|---|---|---|
| One day .. .. .. .. | £4 | £8 |
| Two days .. .. .. | 6 | 10 |
| Three days .. .. .. | 8 | 12 |
| Four days .. .. .. | 9 | 15 |
| Whole week . .. .. | 10 10s. | 20 |

### *Technological Curriculum.*

*Preliminary Year.*—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). French or German. Or the Course for the Preliminary Examination, Victoria University, may be taken.

*First Year.*—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

*Second Year.*—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

*Third Year.*—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

### *Evening Classes.*

Lectures will be given on Chemistry in relation to every-day Industries.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1893, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

## LIVERPOOL COLLEGE OF CHEMISTRY.

*Principal.*—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

## DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

*Professor of Chemistry.*—P. Phillips Bedson, D.Sc., F.I.C., F.C.S.

*Lecturer in Chemistry*—Saville Shaw, F.C.S.

*Lecturer in Agricultural Chemistry.*—R. Greig Smith, B.Sc. (Edin.), F.C.S.

*Assistant Lecturer and Demonstrator.*—F. C. Garrett, M.Sc. (Vict.), F.C.S.

The Session will commence on September 25th, 1893.

1. *General Course.* — This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 4th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry.* — A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Thursday, October 5th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 10th. Fee, £1 1s.

*Metallurgy and Assaying.*—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

*Agricultural Chemistry.*—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, Two Guineas.

*Practical Chemistry.*—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; three days, £3 3s. per term, £8 8s. per session; two days, £2 2s. per term, £5 5s. per session; one day per week, £1 11s. 6d. per term, £3 3s. per session.

*Courses of Study.*—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.
2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

*Associateship in Physical Science.*—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

*Exhibitions.*—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 25th.

*Evening Lectures.*—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

## OWENS COLLEGE,
## VICTORIA UNIVERSITY, MANCHESTER.

*Professor and Director of the Chemical Laboratory.*—Harold B. Dixon, M.A., F.R.S.

*Professor of Organic Chemistry.*—W. H. Perkin, Ph.D., F.R.S.

*Demonstrators and Assistant Lecturers.*—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; and S. H. Davies, B.Sc.

*Lecturer in Dyeing and Printing.*—Ernest Bentz.

*Assistant Lecturer in Metallurgy.*—Gilbert J. Fowler, M.Sc.

The Session begins on October 4, 1892, and ends on June 23, 1893.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

### *General Chemistry.*

*General Chemistry Course.*—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

*Introduction to Organic Chemistry.*—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

*First Year Honours Course.*—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

*Second Year Honours Course.*—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

*Third Year Honours Course.*—At times to be arranged. Physical Chemistry.

*Organic Chemistry* (*General*).—Tuesdays and Thursdays, 9 30, during two Winter Terms.

*Organic Chemistry* (*Honours*).—Mondays and Fridays, 9.30, during the two Winter Terms.

*History of Chemistry and Chemical Philosophy.*—Wednesdays, 10.30, during the Session.

Metallurgy.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: Saturdays, 9.30. The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in three yeare. The Degree of B.Sc. with Honours in Chemistry can also be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Scholarships, &c., are available to students.

### *Technological Chemistry.*

*First Course.*—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

*Second Course.*—The Chemistry of Fuel. The Manuacture of Illuminating Gas and Gaseous Fuel.

*Third Course.*—The Chemistry of Coal Tar.

*Fourth Course.*—Natural and Artificial Dye-stuffs.

*Fifth Course.*—Calico-printing.

### *Certificates in Applied Chemistry.*

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

A combined Lecture and Laboratory Course on the Bleaching, Dyeing, and Printing of Cotton Fabrics is given on Saturdays, at 3, by Mr. Bentz.

## UNIVERSITY COLLEGE, NOTTINGHAM.

### Department of Chemistry, Metallurgy, and Agriculture.

*Professor of Chemistry.*—Frank Clowes, D.Sc. Lond., F.I.C.

*Demonstrators of Chemistry.*—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

*Lecturers.*—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; F. R. Sargeant; M. J. R. Dunstan, M.A., F.R.S.E.; and F. T. Addyman, B,Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1892-93 will be as follows:—First Term, October 9th to December 23rd; Second Term, January 15th to March 31st; Third Term, April 16th to June 30th.

*Lecture Courses.*—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

*Practical Chemistry.*—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees: For one term, £7; for the session, £18; for day students for six hours weekly, 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

*Courses of Technical Chemistry Lectures* are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

*A Pharmaceutical Curriculum* extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), Practical Dispensing, taught by demonstrations and practical work in the laboratory, and Lecture and Laboratory Instruction in Physics.

*Government Lectures and Classes.*—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

*An Agricultural Course* of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

## FIRTH COLLEGE, SHEFFIELD.

*Professor of Chemistry.*—W. Carleton Williams, B.Sc., F.C.S.

*Demonstrators and Assistant Lecturers.*—G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 1st.

*First Year's Course.*—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

*Second Year's Course.*—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

*Third Year's Course.*—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

*Laboratory.*—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

*Evening Classes.*—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

## UNIVERSITY COLLEGE, DUNDEE.

(University of St. Andrews).

*Professor.*— Percy Frankland, Ph.D., B.Sc., F.R.S., &c.

*Assistant Lecturers and Demonstrators.*—F. J. Hambly, F.I.C., J. R. Appleyard, F.C.S., and John Foggie, F.C.S.

The tenth session of the College will be opened on October 10th, 1893.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

### *Lecture Courses.*

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

### *Practical Chemistry (Laboratory).*

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 2 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

*Sessional Fees for Day Students*:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

*Evening Classes.*—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

### *Forster Research Scholarship.*

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

## UNIVERSITY OF EDINBURGH.

### Department of Chemistry.

*Professor.*—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

*Assistants.*—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; W. W. Taylor, M.A.; and A. F. Watson, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

*Lecture Courses.*—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer: it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

*Laboratories.*—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

*Graduation.*—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

## HERIOT-WATT COLLEGE, EDINBURGH.

*Professor.*—John Gibson, Ph.D., F.R.S.E.

*Assistant Professor.*—Arthur W. Bishop, Ph.D.

*Demonstrator.*—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of the systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

## GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Mr. L. H. Cooke, A.R.S.M., formerly Assistant in the Mining Department of the Royal School of Mines, London, has been appointed Lecturer on Mining and Geology at this College. Complete courses of instruction in Metallurgy and Mining will now be given in both Day and Evening Classes.

Copies of the Calendar for 1893-94 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

## UNIVERSITY OF ST. ANDREWS.

### United College of St. Leonard and St. Salvator.

*Professor of Chemistry.* — T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 10th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held in the beginning of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

### *Lecture Courses.*

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

*First Year's Course.*—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a Course of Laboratory Practice of two hours per week, to which Members of the Class are admitted without additional fee.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

*Second Year's Course.*—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

### *Practical Chemistry.*

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly.

## QUEEN'S COLLEGE, BELFAST.

*Professor.*—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st, at 2 p.m. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given during the first or second terms, or from May 1st until the middle of July, as may suit the convenience of the class.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

## QUEEN'S COLLEGE, CORK.

*Professor.*—Augustus E. Dixon, M.D.

*Assistant.*—D. J. O'Mahony, F.C.S.

The College Session begins on October 17th, 1893, and ends on June 9th, 1894. The classes are open to male and female students.

*Systematic Chemistry.*—(1) Inorganic Chemistry; Elementary Organic Chemistry; Chemical Philosophy. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

*Practical Chemistry.*—(1) The General Course of Practical Chemistry, consisting of about forty Lectures of two hours each, begins on January 8th, 1894. (2) A Course for Pharmaceutical Students. (3) Special Courses.—Fee for each Sessional Course, £3.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

## QUEEN'S COLLEGE, GALWAY.

*Professor.*—Alfred Senier, Ph.D., M.D., F.I.C.

The College Session is divided into three terms. The First Term extends from October 17 to December 23, the Second Term from January 8 to March 17, and the Third Term from March 31 to June 12.

The study of Chemistry is pursued throughout the Session by means of experimental lectures and by practice in the laboratory, where each student works independently. Attention is also directed to those technical applications of the science which the wants of the students or the special needs of the West of Ireland appear to demand.

*Theory of Chemistry.*—(1) A General Course of about seventy lectures is given in the First and Second Terms, embracing inorganic and organic chemistry, the non-metallic elements, the atomic theory, the metals, and the synthesis and properties of the more important fatty and aromatic compounds and their probable constitution. (2) A Special Honour Course of about twenty lectures is given in the Third Term. This course is devoted chiefly to organic synthesis, and includes a review of some of the latest researches.

*Experimental Work.*—(1) A General Course of about forty lessons of two hours each is given in the laboratory in the First and Second Terms, embracing the elements of qualitative analysis and the chemical examination of urine. (2) Special Courses of experiments in volumetric and gravimetric analysis, in inorganic and organic preparations, and in the applications of chemistry to medicine and the arts are arranged to meet the requirements of the students.

For prospectuses and further particulars apply to the Registrar.

## ROYAL COLLEGE OF SCIENCE FOR IRELAND,
STEPHEN'S GREEN, DUBLIN.
(SCIENCE AND ART DEPARTMENT).

*Professor of Chemistry.*—W. N. Hartley, F.R.S.

*Assistant Chemist.*—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

*Demonstrator of Chemistry and Assaying.*—E. V. Clark, Associate of the Royal College of Science, London.

The Session commences on Monday, October 2nd, 1893, and ends on June 21st, 1894.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £19; second year, £25; third year, £12.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

NOTE.—Important changes have been made in the Curriculum by which the First Year's Course of study has been simplified. Full particulars are contained in the Directory of the College, which may be had on application to the Secretary.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) Assaying.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

# CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION. — *City and Guilds Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 19th, and the Winter Session opens on Wednesday, October 4th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and Applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 26th, 1893.

Addey's Science and Art School, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day and Evening Classes in Theoretical and Practical Chemistry, &c. The Classes are approved by the County Council.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane. — *Chemistry:* Courses will be conducted, commencing October 2nd, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. G. Chaloner, F.C.S. Lectures — Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6—8 p.m.; Thursdays, 8—10 p.m.; Saturdays, 7—9 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6.30 p.m.; Practical, Wednesdays, 7.30 p.m., Fridays, 6 p.m.

The Central School of Chemistry and Pharmacy, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper. Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

Middlesex College of Chemistry and Pharmacy, 40, Charlotte Street, Portland Place.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

Penywern House Military and Engineering College, Penywern Road, Earl's Court, S.W.

South London School of Pharmacy, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £12 12s.; afterwards £3 3s. per month respectively, inclusive of all departments.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemical Department, Mr. A. G. Bloxam, F.I.C.; Assistant, Mr. H. C. L. Bloxam. Lectures and Practical Classes, also special classes in Chemistry as applied to various arts and industries, are held in the evenings from 7.30—10.0, and are open to both sexes.

People's Palace, Mile End Road, E. (Draper's Company's Institute).—Lecturer, Mr. D. S. Macnair, B.Sc., F.C.S.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry. The Session commences on Monday, September 25th.

Polytechnic Institute, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on October 2nd, 1893.

University Tutorial College, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The large Chemical, Biological, and Physical laboratories opened last Session have been found admirably suited to their purpose, and the proportion of passes in the London University Science Lists has increased rapidly. Students may work either for long or short periods. The Session commences October 2nd, 1893.

Westminster College of Chemistry and Pharmacy, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton. Day and Evening Classes.

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Bristol Medical School.—Mr. T. Coomber, F.C.S.

The Clifton Laboratory, Berkeley Square, Bristol. —Principal, Mr. Ernest H. Cook, D.Sc.Lond., F.I.C., F.C.S.; Assistants, Messrs. H. J. Palmer, F.C.S., S. B. Froude, and J. M. Vaughan. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Every effort is made to produce thorough chemists rather than successful examinees.

Leeds School of Science and Technology, (Mechanics' Institution, Leeds).—Lecturer on Chemistry, Mr. S. J. Harris, M.Sc., F.C.S. Lecturer on Metallurgy, Mr. B. A. Burrell, F.I.C., F.C.S. Lecturer on Physics, Mr. A. Wheatley, B.Sc. Practical Physics and Demonstrator in Chemistry, Mr. H. Holbeche, A.R.C.S. The Chemical Laboratory is open for five evenings, and the Metallurgical Laboratory for two evenings per week. There is a three years' course of lectures in Inorganic Chemistry, and a two years' course in Organic Chemistry and Metallurgy.

Institute of Chemical Technology, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

The Municipal Technical School, Princess Street, Manchester.—Mr. J. H. Reynolds. Day and Evening Classes.

Sheffield Borough Analysts' Laboratory, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

Stockport Technical School.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application.

Technical Institute, Swansea.—Classes in Theoretical and Practical Inorganic Chemistry and Metallurgy, Electricity, Mathematics, &c., from October to May. Principal, W. Morgan, Ph.D., F.C.S., F.I.C.

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Aberdeen University.—Prof. Japp.

School of Medicine (New Veterinary College, Edinburgh).—Mr. Ivison Macadam.

School of Medicine, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, Mr. Paterson, and Drs. Aitken and Readman.

Surgeon's Hall, Nicolson Street, Edinburgh.—Mr. Ivison Macadam. Laboratory work and demonstrations in Agricultural Chemistry. Chemistry Class for Women.

St. Mungo's College and School of Medicine, Edinburgh.—Dr. Milne.

Glasgow University.—Prof. J. Ferguson.

Glasgow Veterinary College.—Professor Cooke.

Anderson's College, Glasgow.—Mr. J. R. Watson.

Laboratory of Science, Painters' Hall, Paisley.—Mr. J. M. B. Taylor. Practical Agricultural Chemistry, October to February inclusive. Practical Botany, Geology, and Mineralogy from March to September.

Royal College of Surgeons in Ireland, Dublin.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

Dublin, Catholic University.—Dr. Campbell.

## CORRESPONDENCE.

### Section B.

### BRITISH ASSOCIATION, NOTTINGHAM MEETING.

*To the Editor of the Chemical News.*

Sir,—I have had several requests from brother chemists to furnish some outline of the Programme for the Chemical Section at the approaching Nottingham Meeting. As far as the order of some of the leading events can be stated, before the meeting of the Sectional Committee, it will be as follows:—President's Address, treating mainly of the "Comparative Chemistry of the Elements," at 12, on Thursday, Sept. 14th; M. Moissan's demonstration of the preparation and properties of Fluorine, Friday, 15th; Bacteriology in its chemical aspects, discussion introduced by Dr. Percy Frankland, Monday, 18th; "Colliery Explosions," discussion introduced by Prof. Harold B. Dixon, Tuesday, 19th. The Sectional proceedings commence at 11 o'clock.—I am, &c.,

Frank Clowes, Hon. Local Sec.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 8, August 21, 1893.

This number contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 12.

**A New Method of Preparing Urea.**—A. Reychler.—The author obtains urea in the wet way by acting upon potassium or ammonium cyanide with an alkaline hypochlorite, and finds the actual yield 89·4 per cent. By Volhard's method, which is very tedious, the yield is only 68 per cent.

**Essential Oil of Eucalyptus.**—G. Bouchardat and Oliveiro.—The oil in question, obtained from specimens of eucalyptus grown in the South of France, appears to be a mixture of various products.

**Chemical Composition of Oil of Niaouli.**—G. Bertrand.—Already inserted.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1764.

# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

## Nottingham, 1893.

## INAUGURAL ADDRESS OF THE PRESIDENT,

J. C. Burdon-Sanderson, M.A., M.D., LL.D., D.C.L., F.R.S., F.R.S.E.,
Professor of Physiology in the University of Oxford.

We are assembled this evening as representatives of the sciences—men and women who seek to advance knowledge by scientific methods. The common ground on which we stand is that of belief in the paramount value of the end for which we are striving, of its inherent power to make men wiser, happier, and better; and our common purpose is to strengthen and encourage one another in our efforts for its attainment. We have come to learn what progress has been made in departments of knowledge which lie outside of our own special scientific interests and occupations, to widen our views, and to correct whatever misconceptions may have arisen from the necessity which limits each of us to his own field of study; and, above all, we are here for the purpose of bringing our divided energies into effectual and combined action.

Probably few of the members of the Association are fully aware of the influence which it has exercised during the last half-century and more in furthering the scientific development of this country. Wide as is the range of its activity, there has been no great question in the field of scientific inquiry which it has failed to discuss; no important line of investigation which it has not promoted; no great discovery which it has not welcomed. After more than sixty years of existence it still finds itself in the energy of middle life, looking back with satisfaction to what it has accomplished in its youth, and forward to an even more efficient future. One of the first of the national associations which exist in different countries for the advancement of science, its influence has been more felt than that of its successors because it is more wanted. The wealthiest country in the world, which has profited more—vastly more—by science than any other, England stands alone in the discredit of refusing the necessary expenditure for its development, and cares not that other nations should reap the harvest for which her own sons have laboured.

It is surely our duty not to rest satisfied with the reflection that England in the past has accomplished so much, but rather to unite and agitate in the confidence of eventual success. It is not the fault of governments, but of the nation, that the claims of science are not recognised. We have against us an overwhelming majority of the community, not merely of the ignorant, but of those who regard themselves as educated, who value science only in so far as it can be turned into money; for we are still in great measure—in greater measure than any other—a nation of shopkeepers. Let us who are of the minority—the remnant who believe that truth is in itself of supreme value, and the knowledge of it of supreme utility—do all that we can to bring public opinion to our side, so that the century which has given Young, Faraday, Lyell, Darwin, Maxwell, and Thomson to England, may before it closes see us prepared to take our part with other countries in combined action for the full development of natural knowledge.

Last year the necessity of an imperial observatory for physical science was, as no doubt many are aware, the subject of a discussion in Section A, which derived its interest from the number of leading physicists who took part in it, and especially from the presence and active participation of the distinguished man who is at the head of the National Physical Laboratory at Berlin. The equally pressing necessity for a central institution for chemistry, on a scale commensurate with the practical importance of that science, has been insisted upon in this Association and elsewhere by distinguished chemists. As regards biology I shall have a word to say in the same direction this evening. Of these three requirements it may be that the first is the most pressing. If so, let us all, whatever branch of science we represent, unite our efforts to realise it, in the assurance that if once the claim of science to liberal public support is admitted, the rest will follow.

In selecting a subject on which to address you this evening I have followed the example of my predecessors in limiting myself to matters more or less connected with my own scientific occupations, believing that in discussing what most interests myself I should have the best chance of interesting you. The circumstance that at the last meeting of the British Association in this town, Section D assumed for the first time the title which it has since held, that of the Section of Biology, suggested to me that I might take the word "Biology" as my starting-point, giving you some account of its origin and first use, and of the relations which subsist between biology and other branches of natural science.

### *Origin and Meaning of the Term "Biology."*

The word "biology," which is now so familiar as comprising the sum of the knowledge which has as yet been acquired concerning living nature, was unknown until after the beginning of the present century. The term was first employed by Treviranus, who proposed to himself as a life-task the development of a new science, the aim of which should be to study the forms and phenomena of life, its origin and the conditions and laws of its existence, and embodied what was known on these subjects in a book of seven volumes, which he entitled "Biology, or the Philosophy of Living Nature." For its construction the material was very scanty, and was chiefly derived from the anatomists and physiologists. For botanists were entirely occupied in completing the work which Linnæus had begun, and the scope of zoology was in like manner limited to the description and classification of animals. It was a new thing to regard the study of living nature as a science by itself, worthy to occupy a place by the side of natural philosophy, and it was therefore necessary to vindicate its claim to such a position. Treviranus declined to found this claim on its useful applications to the arts of agriculture and medicine, considering that to regard any subject of study in relation to our bodily wants—in other words to utility—was to narrow it, but dwelt rather on its value as a discipline and on its surpassing interest. He commends biology to his readers as a study which, above all others, "nourishes and maintains the taste for simplicity and nobleness; which affords to the intellect ever new material for reflection, and to the imagination an inexhaustible source of attractive images."

Being himself a mathematician as well as a naturalist, he approaches the subject both from the side of natural philosophy and from that of natural history, and desires to found the new science on the fundamental distinction between living and non-living material. In discussing this distinction, he takes as his point of departure the constancy with which the activities which manifest themselves in the universe are balanced, emphasising the impossibility of excluding from that balance the vital activities of plants and animals. The difference between vital and physical processes he accordingly finds, not in the nature of the processes themselves, but in their coordination; that is, in their adaptedness to a given purpose, and to the peculiar and special relation in which the organism stands to the external world. All of this is expressed in a proposition difficult to translate into English, in which he defines life as consisting in the reaction of the organism to external influences, and contrasts the uniformity of vital reactions with the variety of their exciting causes.[*]

The purpose which I have in view in taking you back as I have done to the beginning of the century is not merely to commemorate the work done by the wonderfully acute writer to whom we owe the first scientific conception of the science of life as a whole, but to show that this conception, as expressed in the definition I have given you as its foundation, can still be accepted as true. It suggests the *idea of organism* as that to which all other biological ideas must relate. It also suggests, although perhaps it does not express it, that *action* is not an attribute of the organism but of its essence—that if, on the one hand, protoplasm is the basis of life, life is the basis of protoplasm. Their relations to each other are reciprocal. We think of the visible structure only in connection with the invisible process. The definition is also of value as indicating at once the two lines of inquiry into which the science has divided by the natural evolution of knowledge. These two lines may be easily educed from the general principle from which Treviranus started, according to which it is the fundamental characteristic of the organism that all that goes on in it is to the advantage of the whole. I need scarcely say that this fundamental conception of organism has at all times presented itself to the minds of those who have sought to understand the distinction between living and nonliving. Without going back to the true father and founder of biology, Aristotle, we may recall with interest the language employed in relation to it by the physiologists of three hundred years ago. It was at that time expressed by the term *consensus partium*—which was defined as the concurrence of parts in action, of such a nature that each does *quod suum est*, all combining to bring about one effect "as if they had been in secret council," but at the same time *constanti quadam naturæ lege*.[†] Professor Huxley has made familiar to us how a century later Descartes imagined to himself a mechanism to carry out this *consensus*, based on such scanty knowledge as was then available of the structure of the nervous system. The discoveries of the early part of the present century relating to reflex action and the functions of sensory and motor nerves, served to realise in a wonderful way his anticipations as to the channels of influence, afferent and efferent, by which the *consensus* is maintained; and in recent times (as we hope to learn from Professor Horsley's lecture on the physiology of the nervous system) these channels have been investigated with extraordinary minuteness and success.

Whether with the old writers we speak about *consensus*, with Treviranus about *adaptation*, or are content to take *organism* as our point of departure, it means that, regarding a plant or an animal as an organism, we concern ourselves primarily with its activities, or, to use the word which best expresses it, its energies. Now the first thing that strikes us in beginning to think about the activities of an organism is that they are naturally distinguishable into two kinds, according as we consider the action of the whole organism in its relation to the external world or to other organisms, or the action of the parts or organs in their relation to each other. The distinction to which we are thus led between the *internal* and *external* relations of plants and animals has of course always existed, but has only lately come into such prominence that it divides biologists more or less completely into two camps,—on the one hand those who make it their aim to investigate the actions of the organism and its parts by the accepted methods of physics and chemistry, carrying this investigation as far as the conditions under which each process manifests itself will permit; on the other, those who interest themselves rather in considering the place which each organism occupies, and the part which it plays in the economy of Nature. It is apparent that the two lines of inquiry, although they equally relate to what the organism *does*, rather than to what it *is*, and therefore both have equal right to be included in the one great science of life, or biology, yet lead in directions which are scarcely even parallel. So marked, indeed, is the distinction that Prof. Haeckel some twenty years ago proposed to separate the study of organisms with reference to their place in Nature under the designation of "Œcology," defining it as compromising "the relations of the animal to its organic as well as to its inorganic environment, particularly its friendly or hostile relations to those animals or plants with which it comes into direct contact.[*] Whether this term expresses it or not, the distinction is a fundamental one. Whether with the œcologist we regard the organism in relation to the world, or with the physiologist as a wonderful complex of vital energies, the two branches have this in common, that both studies fix their attention, not on stuffed animals, butterflies in cases, or even microscopical sections of the animal or plant body,—all of which relate to the framework of life, — but on life itself.

The conception of biology which was developed by Treviranus as far as the knowledge of plants and animals which then existed rendered possible, seems to me still to express the scope of the science. I should have liked, had it been within my power, to present to you both aspects of the subject in equal fulness; but I feel that I shall best profit by the present opportunity if I derive my illustrations chiefly from the division of biology to which I am attached—that which concerns the *internal* relations of the organism, it being my object not to specialise in either direction, but, as Treviranus desired to do, to regard it as part—surely a very important part—of the great science of Nature.

The origin of life, the first transition from non-living to living, is a riddle which lies outside of our scope. No seriously-minded person, however, doubts that organised nature, as it now presents itself to us, has become what it is by a process of gradual perfecting or advancement, brought about by the elimination of those organisms which failed to obey the fundamental principle of adaptation which Treviranus indicated. Each step, therefore, in this evolution is a reaction to external influences, the motive of which is essentially the same as that by which from moment to moment the organism governs itself. And the whole process is a necessary outcome of the fact that those organisms are most prosperous which look best after their own welfare. As in that part of biology which deals with the internal relations of the organism, the interest of the individual is in like manner the sole motive by which every energy is guided. We may take what Treviranus called *selfish* adaptation—*Zweckmässigkeit für sich selber*—as a connecting link between the two branches of biological study. Out of this relation springs another which I need not say was not recognised until after the Darwinian epoch—that, I mean, which subsists between the two evolutions, that of the race and that of the individual. Treviranus, no less distinctly than his great contemporary Lamarck, was well aware that the affinities of plants and animals must be estimated according to their developmental value, and consequently that classifi-

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[*] "Leben besteht in der Gleichförmigkeit der Reaktionen bei ungleichförmigen Einwurkungen der Aussenwelt." — Treviranus, "Biologie oder Philosophie der lebenden Natur," Göttingen, 1802, vol. i., p. 83.

[†] Bausner, "De Consensu Partium Humani Corporis," Amst., 1556, Præf. ad lectorem, p. 4.

[*] These he identifies with "those complicated mutual relations which Darwin designates as conditions of the struggle for existence." Along with chorology—the distribution of animals—œcology constitutes; what he calls *Relations physiologie.* Haeckel, "Entwickelungsgang n. Aufgaben der Zoologie," *Jenaische Zeitsch*, vol. v, 1869, p. 353

cation must be founded on development; but it occurred to no one what the real link was between descent and development; nor was it, indeed, until several years after the publication of the "Origin" that Haeckel enunciated that "biogenetic law" according to which the development of any individual organism is but a memory, a recapitulation by the individual of the development of the race—of the process for which Fritz Müller had coined the excellent word "phylogenesis"; and that each stage of the former is but a transitory reappearance of a bygone epoch in its ancestral history. If, therefore, we are right in regarding ontogenesis as dependent on phylogenesis, the origin of the former must correspond with that of the latter; that is, on the power which the race or the organism at every stage of its existence possesses of profiting by every condition or circumstance for its own advancement.

From the short summary of the connection between different parts of our science you will see that biology naturally falls into three divisions, and these are even more sharply distinguished by their methods than by their subjects; namely, *Physiology*, of which the methods are entirely experimental; *Morphology*, the science which deals with the forms and structure of plants and animals, and of which it may be said that the body is anatomy,—the soul, development; and finally *Œcology*, which uses all the knowledge it can obtain from the other two, but chiefly rests on the exploration of the endless varied phenomena of animal and plant life as they manifest themselves under natural conditions. This last branch of biology—the science which concerns itself with the external relations of plants and animals to each other, and to the past and present conditions of their existence—is by far the most attractive. In it those qualities of mind which especially distinguish the naturalist find their highest exercise, and it represents more than any other branch of the subject what Treviranus termed the "philosophy of living nature." Notwithstanding the very general interest which several of its problems excite at the present moment, I do not propose to discuss any of them, but rather to limit myself to the humbler task of showing that the fundamental idea which finds one form of expression in the world of living beings regarded as a whole—the prevalence of the best—manifests itself with equal distinctness, and plays an equally essential part in the internal relations of the organism in the great science which treats of them—Physiology.

### *Origin and Scope of Modern Physiology.*

Just as there was no true philosophy of living nature until Darwin, we may with almost equal truth say that physiology did not exist as a science before Johannes Müller. For although the sum of his numerous achievements in comparative anatomy and physiology, notwithstanding their extraordinary number and importance, could not be compared for merit and fruitfulness with the one discovery which furnished the key to so many riddles, he, no less than Darwin, by his influence on his successors was the beginner of a new era.

Müller taught in Berlin from 1833 to 1857. During that time a gradual change was in progress in the way in which biologists regarded the fundamental problem of life. Müller himself, in common with Treviranus and all the biological teachers of his time, was a vitalist, *i. e.*, he regarded what was then called the *vis vitalis*—the *Lebenskraft*—as something capable of being correlated with the physical forces; and as a necessary consequence held that phenomena should be classified or distinguished, according to the forces which produced them, as vital or physical, and that all those processes—that is, groups or series of phenomena in living organisms—for which, in the then very imperfect knowledge which existed, no obvious physical explanation could be found, were sufficiently explained when they were stated to be dependent on so-called vital laws. But during the period of Müller's greatest activity times were changing, and he was changing with them. During his long career as Professor at Berlin he became more and more objective in his tendencies, and exercised an influence in the same direction on the men of the next generation, teaching them that it was better and more useful to observe than to philosophise; so that, although he himself is truly regarded as the last of the vitalists,—for he was a vitalist to the last,—his successors were adherents of what has been very inadequately designated the mechanistic view of the phenomena of life. The change thus brought about just before the middle of this century was a revolution. It was not a substitution of one point of view for another, but simply a frank abandonment of theory for fact, of speculation for experiment. Physiologists ceased to theorise because they found something better to do. May I try to give you a sketch of this era of progress?

Great discoveries as to the structure of plants and animals had been made in the course of the previous decade, those especially which had resulted from the introduction of the microscope as an instrument of research. By its aid Swann had been able to show that all organised structures are built up of those particles of living substance which we now call cells, and recognise as the seats and sources of every kind of vital activity. Hugo Mohl, working in another direction, had given the name "protoplasm" to a certain hyaline substance which forms the lining of the cells of plants, though no one as yet knew that it was the essential constituent of all living structures—the basis of life no less in animals than in plants. And, finally, a new branch of study—histology—founded on observations which the microscope had for the first time rendered possible, had come into existence. Bowman, one of the earliest and most successful cultivators of this new science, called it physiological anatomy,* and justified the title by the very important inferences as to the secreting function of epithelial cells and as to the nature of muscular contraction, which he deduced from his admirable anatomical researches. From structure to function, from microscopical observation to physiological experiment, the transition was natural. Anatomy was able to answer some questions, but asked many more. Fifty years ago physiologists had microscopes, but had no laboratories. English physiologists—Bowman, Paget, Sharpey—were at the same time anatomists; and in Berlin Johannes Müller, along with anatomy and physiology, taught comparative anatomy and pathology. But soon that specialisation which, however much we may regret its necessity, is an essential concomitant of progress, became more and more inevitable. The structural conditions on which the processes of life depend had become, if not known, at least accessible to investigation; but very little indeed had been ascertained of the nature of the processes themselves,—so little indeed that if at this moment we could blot from the records of physiology the whole of the information which had been acquired, say in 1840, the loss would be difficult to trace,—not that the previously-known facts were of little value, but because every fact of moment has since been subjected to experimental verification. It is for this reason that, without any hesitation, we accord to Müller, and to his successors Brücke, du Bois-Reymond, Helmholtz, who were his pupils, and Ludwig in Germany, and to Claude Bernard† in France, the title of founders of our science. For it is the work which they began at that remarkable time (1845—55), and which is now being carried on by their pupils or their pupils' pupils in England, America, France, Germany, Denmark, Sweden, Italy, and even in that youngest contributor to the advancement of science, Japan, that physiology has been gradually built up to whatever completeness it has at present attained.

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* The first part of the *Physiological Anatomy* appeared in 1843. It was concluded in 1856.

† It is worthy of note that these five distinguished men were nearly contemporaneous! Ludwig graduated in 1839, Bernard in 1843, the other three between those dates. Three survive—Helmholtz, Ludwig, du Bois-Reymond.

What were the conditions which brought about this great advance which coincided with the middle of the century? There is but little difficulty in answering the question. I have already said that the change was not one of doctrine, but of method. There was, however, a leading idea in the minds of those who were chiefly concerned in bringing it about. That leading notion was that, however complicated may be the conditions under which vital energies manifest themselves, they can be split into processes which are identical in nature with those of the non-living world, and, as a corollary to this, that the analysing of a vital process into its physical and chemical constituents, so as to bring these constituents into measurable relation with physical or chemical standards, is the only mode of investigating them which can lead to satisfactory results.

There were several circumstances which at that time tended to make the younger physiologists (and all of the men to whom I have just referred were then young) sanguine, perhaps too sanguine, in the hope that the application of experimental methods derived from the exact sciences would afford solutions of many physiological problems. One of these was the progress which had been made in the science of chemistry, and particularly the discovery that many of the compounds which before had been regarded as special products of vital processes could be produced in the laboratory, and the more complete knowledge which had been thereby acquired of their chemical constitutions and relations. In like manner the new school profited by the advances which had been made in physics, partly by borrowing from the physical laboratory various improved methods of observing the phenomena of living beings, but chiefly in consequence of the direct bearing of the crowning discovery of that epoch (that of the conservation of energy) on the discussions which then took place as to the relations between vital and physical forces; in connection with which it may be noted that two of those who (along with Mr. Joule and your President at the last Nottingham meeting) took a prominent part in that discovery—Helmholtz and J. R. Mayer—were physiologists as much as they were physicists. I will not attempt even to enumerate the achievements of that epoch of progress. I may, however, without risk of wearying you, indicate the lines along which research at first proceeded, and draw your attention to the contrast between then and now. At present a young observer who is zealous to engage in research finds himself provided with the most elaborate means of investigation, the chief obstacle to his success being that the problems which have been left over by his predecessors are of extreme difficulty, all of the easier questions having been worked out. There were then also difficulties, but of an entirely different kind. The work to be done was in itself easier, but the means for doing it were wanting, and every investigator had to depend on his own resources. Consequently the successful men were those who, in addition to scientific training, possessed the ingenuity to devise and the skill to carry out methods for themselves. The work by which du Bois-Reymond laid the foundation of animal electricity would not have been possible had not its author, besides being a trained physicist, knows how to do as good work in a small room in the upper floor of the old University Building at Berlin as any which is now done in his splendid laboratory. Had Ludwig not possessed mechanical aptitude, in addition to scientific knowledge, he would have been unable to devise the apparatus by which he measured and recorded the variations of arterial pressure (1848), and verified the principles which Young had laid down thirty years before as to the mechanics of the circulation. Nor, lastly, could Helmholtz, had he not been a great deal more than a mere physiologist, have made those measurements of the time-relations of muscular and nervous responses to stimulation, which not only afford a solid foundation for all that has been done since in the same direction, but have served as models of physiological experiment, and as evidence that perfect work was possible and was done by capable men, even when there were no physiological laboratories.

Each of these examples relates to work done within a year or two of the middle of the century.* If it were possible to enter more fully on the scientific history of the time, we should, I think, find the clearest evidence, first, that the foundation was laid in anatomical discoveries, in which it is gratifying to remember that English anatomists (Allen Thomson, Bowman, Goodsir, Sharpey) took considerable share; secondly, that progress was rendered possible by the rapid advances which, during the previous decade, had been made in physics and chemistry, and the participation of physiology in the general awakening of the scientific spirit which these discoveries produced. I venture, however, to think that, notwithstanding the operation of these two causes, or rather combinations of causes, the development of our science would have been delayed had it not been for the exceptional endowments of the four or five young experimenters whose names I have mentioned, each of whom was capable of becoming a master in his own branch, and of guiding the future progress of inquiry.

Just as the affinities of an organism can be best learned from its development, so the scope of a science may be most easily judged of by the tendencies which it exhibits in its origin. I wish now to complete the sketch I have endeavoured to give of the way in which physiology entered on the career it has since followed for the last half-century, by a few words as to the influence exercised on general physiological theory by the progress of research. We have seen that no real advance was made until it became possible to investigate the phenomena of life by methods which approached more or less closely to those of the physicist, in exactitude. The methods of investigation being physical or chemical, the organism itself naturally came to be considered as a complex of such processes, and nothing more. And in particular the idea of adaptation, which, as I have endeavoured to show, is not a consequence of organism, but its essence, was in great measure lost sight of. Not, I think, because it was any more possible than before to conceive of the organism otherwise than as a working together of parts for the good of the whole, but rather that, if I may so express it, the minds of men were so occupied with new facts that they had not time to elaborate theories. The old meaning of the term "adaptation" as the equivalent of "design" had been abandoned, and no new meaning had yet been given to it, and consequently the word "mechanism" came to be employed as the equivalent of "process," as if the constant concomitance or sequence of two events was in itself a sufficient reason for assuming a mechanical relation between them. As in daily life so also in science, the misuse of words leads to misconceptions. To assert that the link between *a* and *b* is mechanical, for no better reason than that *b* always follows *a*, is an error of statement, which is apt to lead the incautious reader or hearer to imagine that the relation between *a* and *b* is understood, when in fact its nature may be wholly unknown. Whether or not at the time which we are considering, some physiological writers showed a tendency to commit this error, I do not think that it found expression in any generally accepted theory of life. It may, however, be admitted that the rapid progress of experimental investigation led to too confident anticipations, and that to some enthusiastic minds it appeared as if we were approaching within measurable distance of the end of knowledge. Such a tendency is, I think, a natural result of every signal advance. In an eloquent Harveian oration, delivered last autumn by Dr. Bridges, it was indicated how, after Harvey's great discovery of the circulation, men were too apt to found upon it explanations of all phenomena

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* The *Untersuchungen über thierische Electricität* appeared in 1848; Ludwig's researches on the circulation, which included the first description of the "kymograph" and served as the foundation of the "graphic method" in 1847; Helmholtz's research on the propagation in motor nerves in 1851.

whether of health or disease, to such an extent that the practice of medicine was even prejudicially affected by it. In respect of its scientific importance the epoch we are considering may well be compared with that of Harvey, and may have been followed by an undue preference of the new as compared with the old, but no more permanent unfavourable results have shown themselves. As regards the science of medicine, we need only remember that it was during the years between 1845 and 1860 that Virchow made those researches by which he brought the processes of disease into immediate relation with the normal processes of cell development and growth, and so, by making pathology a part of physiology, secured its subsequent progress and its influence on practical medicine. Similarly in physiology, the achievements of those years led on without any interruption or drawback to those of the following generation; while in general biology, the revolution in the mode of regarding the internal processes of the animal or plant organism which resulted from these achievements, prepared the way for the acceptance of the still greater revolution which the Darwinian epoch brought about in the views entertained by naturalists of the relations of plants and animals to each other and to their surroundings.

It has been said that every science of observation begins by going out botanising, by which, I suppose, is meant that collecting and recording observations is the first thing to be done in entering on a new field of inquiry. The remark would scarcely be true of physiology, even at the earliest stage of its development, for the most elementary of its facts could scarcely be picked up as one gathers flowers in a wood. Each of the processes which go to make up the complex of life requires separate investigation, and in each case the investigation must consist in first splitting up the process into its constituent phenomena, and then determining their relation to each other, to the process of which they form part, and to the conditions under which they manifest themselves. It will, I think, be found that even in the simplest inquiry into the nature of vital processes some such order as this is followed. Thus, for example, if muscular contraction be the subject on which we seek information, it is obvious that, in order to measure its duration, the mechanical work it accomplishes, the heat wasted in doing it, the electromotive forces which it develops, and the changes of form associated with these phenomena, special modes of observation must be used for each of them, that each measurement must be in the first instance separately made, under special conditions, and by methods specially adapted to the required purpose. In the synthetic part of the inquiry the guidance of experiment must again be sought for the purpose of discriminating between apparent and real causes, and of determining the order in which the phenomena occur. Even the simplest experimental investigations of vital processes are beset with difficulties. For, in addition to the extreme complexity of the phenomena to be examined and the uncertainties which arise from the relative inconstancy of the conditions of all that goes on in the living organism, there is this additional drawback, that, whereas in the exact sciences experiment is guided by well-ascertained laws, here the only principle of universal application is that of adaptation, and that even this cannot, like a law of physics, be taken as a basis for deductions, but only as a summary expression of that relation between external exciting causes and the reactions to which they give rise, which, in accordance with Treviranus's definition, is the essential character of vital activity.

(To be continued).

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**Rapid Determination of Extract in Wine.**—Medicus evaporates 5 c.c. of wine in a tared watch-glass, and dries it for thirty minutes in a water drying stove. Sweet wines must first be diluted to ten times their volume.—*Zeit. Anal. Chem.*, xxxii., Part 3.

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ON THE

# ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 100).

### *Products Obtained in Presence of a Large Excess of Caustic Alkali* (60° C.).

Solutions were set up exactly of the same strength as those used in the preparation of the red-violet precipitate, excepting that the quantity of alkali was increased four times; and the process followed was precisely the same, excepting that the quantity of iodine solution added was lessened by a half.

In this case no precipitate was formed until after acidification, when a white precipitate was obtained, which consisted of soft satiny needle-shaped crystals having a low melting-point and constituted for the most part of true substituted phenols. The melting-point of a similarly prepared precipitate was before given as 65° C.

Total iodine of the whole precipitate:—
Quantity taken =0·2852 grm.
Silver iodide found =0·3753 „ =71·10 p.c. iodine.

A quantity of the precipitate was dissolved in chloroform and allowed to evaporate slowly in a flat dish, when the precipitate was found to be deposited in two pretty distinct circles. The inner constituted only a very small portion, was definitely crystallised in somewhat tabular form, and melted at a fairly high temperature; whilst the outer circle crystallised much less distinctly in the needle-shaped form, and melted about 66° C. This outer portion was re-deposited from ether, and the outer circle again taken. When this is deposited from solution in ether, a little free iodine becomes apparent at the moment of deposition, but it may be crystallised colourless from alcohol.

Total iodine of this portion:—
Quantity taken =0·1769 grm.
Silver iodide found =0·2401 „ =73·33 p.c. iodine.
Melting-point 66° C.

This was therefore taken to be a di-iodophenol, the theoretical iodine percentage being 73·41. The melting-point given for a di-iodophenol in "Watts' Dictionary" is 68° C., but no other evidence is given which could be used for identification or criticism. However, the above method of preparation is simpler, and the product less liable to contamination with disturbing isomers and products of different substitution degree than any of the published methods of preparing the di-iodophenols. It may be remarked here, however, that throughout the classes of compounds dealt with in this paper, the presence of a mere trace of free iodine greatly disturbs the melting-point of any individual member. This is the more conspicuous in the oxidised class, of which this paper more particularly treats, in that they combine with iodine which is not free in the ordinary sense, but which is free relative to the true state of substitution.

### *Products Obtained at the Ordinary Temperature.*

The process and quantities used were the same as those employed in the preparation of the red-violet precipitate, excepting that no heat was applied (temperature 14° C.). No precipitate was formed until after acidification, when a white pulverulent precipitate was obtained. This precipitate was distilled in a current of steam. A considerable portion passed over and remained soluble in the hot water, slowly crystallising out as the water cooled.

This was collected and dried, when it appeared in the form of white satiny needles, quite similar to the white compound examined in the last case when slowly crystallised, with odour less pronounced. Melting-point 72° C.

Total iodine of this distillate :—
Quantity taken =0·0977 grm.
Silver iodide found=0·1330 ,, =73·55 p.c. iodine.

This, therefore, was also a di-iodophenol. The melting-point agrees with that given in "Watts' Dictionary" for a di-iodophenol.

The residue which remained from the distillate was dissolved out by ether, from which it was recovered in the form of a caked mass, partly crystalline and of a slightly reddish colour, due to liberation of iodine. It was fairly soluble in alcohol, from which it crystallised in brittle white needles, which on exposure to air showed free iodine.

Total iodine of this residue :—
Quantity taken =0·1658 grm.
Silver iodide found=0·2405 ,, =78·37 p.c. iodine.
Combustion of same :—
Quantity taken =0·1491 grm.
Water found =0·0126 ,, = 0·94 p.c. hydrogen.
Carbon dioxide found =0·0813 ,, =14·87 p.c. carbon.

The melting-point was taken, when it was observed that a portion melted about 135° C., in which the remainder seemed to dissolve. A small portion was therefore heated over this temperature in an open basin until volatilisation was scarcely perceptible, and the remaining portion was then allowed to solidify. Heat was again applied, when it was observed to melt about 145° C. The remainder of the residue was therefore treated similarly, and the less volatile portion remaining was then taken for analysis.

Total iodine :—
Quantity taken =0·1898 grm.
Silver iodide found=0·2785 ,, =79·27 p.c. iodine.

The remainder was then still further heated until only a very small portion remained, which was taken for analysis.

Total iodine :—
Quantity taken =0·0816 grm.
Silver iodide found=0·1176 ,, =77·86 p.c. iodine.
Combustion of same :—
Quantity taken =0·1550 grm.
Water found =0·0124 ,, = 0·88 p.c. hydrogen.
Carbon dioxide found =0·0818 ,, =14·39 p.c. carbon.

This is sufficient to show that the residue from the distillation was not a mere mixture of a tri-derivative with others of lower substitution, but that oxidation had also taken place in this case. What was volatilised must have been a mixture of di- and tri-substituted phenols.

### *Relative to Messinger and Vortman's Paper on the Red-Violet Compounds.*

It would be somewhat uncharitable to criticise the remarks occurring in their paper regarding the composition and constitution of the red phenol compounds obtained by them, since they are given very provisionally. Nevertheless it must be remembered that three years have elapsed since its publication. The criticism might indeed be put into a nutshell by simply stating that they failed to recognise that the precipitate was a complex one, and contained iodine other than that of substitution. However, the following abstract will be of service, and is needful in order to show their train of thought and experimental evidence adduced :—

It is described as violet-coloured, insoluble in water and dilute acids, soluble with red colour in alcohol, readily soluble in ether, benzol, and chloroform. When distilled in a current of steam it loses its red colour, the distillate contains free iodine, and, on standing, deposits a small quantity of a body in white needles melting at from 138° to 140° C. They think probably this is a di-iodophenol. When the red iodophenol is boiled with caustic potash it is changed to a bright reddish white colour, and loses a large part. When the alkaline filtrate is acidified the solution deposits a white substance melting at 154° to 156° C., corresponding to a tri-iodophenol. The filtrate from the latter is free from iodine. Total iodine found in this white precipitate = 80·8 per cent. This they take to be the tri-iodophenol already known, whilst the red compound they consider to be an isomer. They would represent the red compound as di-iodophenol-iodide, $C_6H_3I_2.OI$, having regard to its conversion into tri-iodophenol by potash as above, as also its splitting into iodine and di-iodophenol.

(To be continued.)

## ON THE DETERMINATION OF VANADIC ACID.*

By Herren A. DITTE, CARNOT, MANASSE, and ERICSHEIM.

(Concluded from p. 102).

THE solution is placed in a weighed platinum capsule, evaporated, the residue of the hydrated vanadic acid which has remained in the porcelain capsule is dissolved in a minimum of ammonia, added to the main quantity, again evaporated, dried on the air-bath at 120°, and then heated in the oxidising flame with access of air, at first avoiding fusion, and the mass when ultimately fused is distributed as much as possible over the sides of the crucible by shaking round. When cold it appears (except in a few dark spots) reddish-brown, coarsely crystalline, with the characteristic structure of pure melted vanadic acid, and contains only traces of tungstic acid (1-10th to 2-10ths per cent of $WO_3$ in the total quantity). To determine it the contents of the crucible, after weighing, are treated with a gentle heat with dilute sulphuric acid and sulphurous acid, when all the vanadium is dissolved as vanadyl sulphate. The trifling residue of tungstic acid which is left is washed with dilute sulphuric acid after filtration, and weighed. The solution of vanadium is evaporated, the sulphuric acid is driven off, and the residue ignited as above, when vanadic acid is obtained which becomes quite homogeneous on fusion. Vanadic acid must *not* be melted in porcelain vessels; otherwise, on dissolving in sulphuric or sulphurous acids, there is left a yellow residue, formed by the action of vanadic acid upon the glaze, and probably containing silico-vanadic acid.

The fixed alkalies present may be determined in a simple manner in the solution filtered off from the mercurial salts of the acids. The mercury is removed by means of sulphuretted hydrogen, and the alkali determined as sulphate, converting the acid sulphates into normal salts by heating in a current of air charged with ammonia, as indicated by G. Krüss (*Berichte*, xx., 1682).

If this method of analysis is to be applied to metatungstates they must first be converted into normal tungstates by boiling and repeated evaporation with ammonia. The solution, freed from excess of ammonia, is then precipitated as already explained. Salts of lead and silver are best decomposed with extremely dilute solution of sodium chloride; the remaining metallic and earthy alkaline salts are decomposed by repeated fusion with sodium-potassium carbonate; the united alkaline solutions are to be neutralised at a gentle heat with acetic acid, and precipitated as above directed.

It must be especially pointed out that the reagents used

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* *Zeitschrift fur Analytische Chemie.*

must be purified with the utmost care. All fixed residues from the mercurial salt, the hydrochloric acid, the nitric acid, and the ammonia would be found in the vanadic acid, in which case it melts either with great difficulty or not at all.

G. Krüss and K. Ohnmais used Friedheim's method in the analysis of the various vanadium sulpho-salts, and obtained very satisfactory results (*Liebig's Annalen*, 263, 39), both in the determination of the vanadic acid and of the fixed alkalies.

For the detection and determinatson of vanadium in rocks and ores L. l'Hôte utilises the volatility of vanadium oxychloride (*Comptes Rendus*, civ., 990).

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 101).

### B. *With Especial Apparatus.*

The leading idea in the design of the new spectral apparatus which my next photographs required was the utmost possible reduction of the resistance of the air. My reflections had led me to three different constructions, according to which the stratum of air was to be reduced either diminishing the focal distance or by exhausting the tubes of the collimator and the camera, whilst retaining the original focal distance, or by exhausting the entire spectrum apparatus.

The entire removal of the air from the track of the rays in the apparatus would certainly ensure the most favourable result conceivable, if the desired object is attainable in this manner. But the difficulties of obtaining such a spectrum apparatus, exhausted of air in the manner of Geissler tubes, seemed so considerable that I even renounced the less serious project of partial exhaustion, and decided on the diminution of the focal distance.

A very short focal distance yields, if a single quartz prism is employed, spectra of a minute length. Spectra rich in lines, such as that of the sun, are then no longer capable of resolution. For such photographs the apparatus is almost useless. This applies more to the visible spectrum than to the ultra-violet; and in the most refrangible part of the ultra-violet, where the lines, according to their wave-length, are relatively much more remote from each other than in the less refrangible part, the conditions are still more favourable. Here therefore, as I show below, the resolution of densely crowded lines, which in such cases are decisive, can be effected with microscopical minuteness, even with a very small apparatus.

An increase of dispersion by means of a greater number of prisms cannot be admitted, on account of the loss of light involved. The result of the experiment depends in the first place upon preserving the energy of the rays.

In order that the proofs, in spite of their smallness, might meet the most severe demands, everything was done which could promote the sharpness and distinctness of the image, both in the construction of the apparatus and in the selection and arrangement of the auxiliary apparatus required for taking the photograph.

Concerning the measurement of the focal distance I have remained for a long time undecided, as all the data for the effects of a greater or less reduction of the length of the tube were wanting. The numerical values which Cornu has established for the absorption of the most refrangible rays in the air were here unsuitable, from the reason mentioned. So much only seemed certain that a moderate decrease of the length of the tube would scarcely lead to a decisive result. Proceeding from the assumption that the greater energy of the rays, and in like manner the complete sharpness of the image, were connected with a smaller length of the tube, and that a small but sharply defined image was preferable to one large but less clear, I selected a lens of only 150 m.m. focal distance.

*The Photographic Spectrum Apparatus.*

Its optical part consists of a double prism of 60°, with a square aperture of 30 m.m., and of two plano-convex quartz lenses of 150 m.m. focal distance (D, 589) and 26 m.m. diameter.

The optician Herr B. Halle, to whose kindness I am indebted for these lenses, has used the greatest care in the selection of the material and in its elaboration. How greatly this circumstance favoured the sharpness of the proofs I did not learn until I compared proofs taken with another pair of lenses of a different origin.

The two halves of the prism are joined together with a very thin layer of glycerine.

The mechanical part of the apparatus consists of a strong tripod fitted with levelling screws, which supports on a strong pillar a disc of 18 c.m. in diameter, capable of revolving on its centre, upon which are fixed the collimator, the support of the prism, and the camera, so as to be capable of adjustment. The slide of the slit has cast-steel cheeks and a micrometer screw, the drum of which allows of readings down to 0·002 m.m. It is connected with the collimator by means of a very accurately-executed draw-tube. with which also the plate is focussed. That this is effected with the collimator, and not also with the camera, is because the entire camera is built of glass, and is not adapted for drawing out. The support of the prism has adjustments necessary for levelling the prism (the Gauss eyepiece), and for adjustment to the minimum of deflection. A piece of velvet is suspended over the prism to exclude extraneous light.

The camera is the only peculiar feature in the apparatus. Except the case, it is built of mirror-glass, and —with the exception of a small metal screw-clamp, serving to secure the track of the case—there is in the entire camera not a single screw-joint. The case can revolve on the medium line of the photographic plate, so that the plate can take any desired angle with the axis of the lens between 20 and 32°. The lens is secured directly to the glass body of the camera. Two openings, which the case in consequence of its mobility forms with the body of the camera, are closed with velvet. A glass junction, which I would here have used in preference, was impracticable. The oblique position of the plate can be read off on a roughly-graduated arc. The body of the camera is of a parallelepipedal shape, and is supported by an arm of strong mirror-glass. prolonged at right angles on its long side. The prolongation of the arm effects the connection of the camera with the rotatory disc of the apparatus, for which purpose the latter bears two powerful clamps.

(To be continued.)

**The Chemical Laboratory of Wiesbaden.**—In the Summer Term, 1893, there were fifty-seven students on the books. Of these, thirty-six were from Germany, five from Austro-Hungary, four from Russia, four from North America, three from Sweden and Norway, one from Holland, one from Belgium, one from France, one from Spain, and one from Batavia. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, and architect J. Brahm. The assistants in the instruction laboratory were three in number, in the private laboratory eighteen, and in the Versuchsstation two. The next Winter Term begins the 16th of October. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation, on behalf of manufacture, trade, mining, agriculture, and hygiene.

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, June 15th, 1893.*

Dr. Armstrong, President, in the Chair.

(Concluded from p. 109).

47. "*The Colouring-matter of Drosera Whittakeri.*" (II.). By E. Rennie, M.A., D.Sc.

In a previous communication (*C. S. Trans.*, 1889, 371), the author has described two colouring-matters separated from *D. Whittakeri*, which he believed to be derivatives of methylnaphthaquinone. He now confirms the formula $C_{11}H_8O_5$ previously assigned to the less soluble and more abundant constituent; a determination of its molecular weight, by Raoult's cryoscopic method, gave the value 223, the calculated value being 220. When boiled with a solution of sodium carbonate, this substance yields reddish brown crystals of a mono-sodium derivative, $C_{11}H_7O_5Na{\cdot}2H_2O$, from which the corresponding calcium derivative was prepared; it also yields a disodium derivative. Two yellow crystalline acetyl derivatives were obtained from it, one melting at 154°, the other at 138°, the former being a triacetate, and the latter a compound of the triacetate with acetic acid.

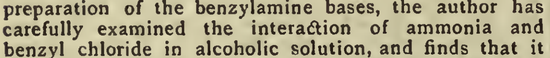
The formula $C_{11}H_8O_4$ previously assigned to the more soluble substance is confirmed; it yields a diacetate. Hitherto this substance has always been obtained in red crystals; in an experiment in which a small quantity was incompletely oxidised, a portion was recovered in the form of yellow crystals melting at 178°, and the author is therefore inclined to think that the pure substance is yellow.

48. "*Preparation of Mono-, Di-, and Tri-Benzylamine.*" By Arthur T. Mason, Ph.D.

No good method having as yet been published for the preparation of the benzylamine bases, the author has carefully examined the interaction of ammonia and benzyl chloride in alcoholic solution, and finds that it takes place without application of heat and is complete in four or five days. If the theoretical quantity of ammonia be used, tribenzylamine is the principal product, the primary and secondary amines being formed in very small quantity; whereas when a large excess of ammonia (20 mols. to 1 mol. of chloride) is used, mono- and dibenzylamine form the chief products, tribenzylamine appearing in small quantity. The details of the process have been worked out, as also an easy method for the separation of the three amines based on the difference in solubility in water of the chlorhydrides. Dibenzylamine has been prepared for the first time by distillation under reduced pressure: it is a colourless liquid distilling without undergoing the slightest decomposition at 188—189° under 35 m.m. pressure.

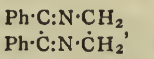
49. "*Piazine* (*Pyrazine*) *Derivatives.*" (II.) By Arthur T. Mason, Ph.D.

A continuation of previous researches (*C. S. Trans.*, 1889, 97; *Ber.*, xx., 267), having reference to the constitution of the compounds resulting from the interaction of ethylene diamine and orthodiketones. The first product from benzil and ethylenediamine is not a true piazine, being easily re-converted into its generators by dilute chlorhydric acid:—



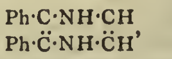
$$\begin{array}{l}Ph{\cdot}CO\\Ph{\cdot}\dot{C}O\end{array} + \begin{array}{l}CH_2{\cdot}NH_2\\\dot{C}H_2{\cdot}NH_2\end{array} = \begin{array}{l}Ph{\cdot}C{:}N{\cdot}CH_2\\Ph{\cdot}\dot{C}{:}N{\cdot}\dot{C}H_2\end{array} + 2H_2O.$$

When heated above its melting-point, this compound (so-called) (2, 3) diphenylpiazine (5, 6) dihydride yields two true piazine derivatives, which are not resolved into their generators by dilute chlorhydric acid; one of these compounds is isomeric with the (5, 6) dihydride, and is formed by a molecular transformation of that substance: it contains two imide (NH) groups, and is a strong base, being very soluble in dilute chlorhydric acid; it is very easily oxidised, and even when dissolved in chlorhydric acid saturated with carbon dioxide changes spontaneously into the final product of interaction—(2, 3) diphenylpiazine. In the author's opinion, these facts can only be explained by assuming that the true piazines contain a para-bond, thus—



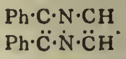
$$\begin{array}{l}Ph{\cdot}C{:}N{\cdot}CH_2\\Ph{\cdot}\dot{C}{:}N{\cdot}\dot{C}H_2\end{array},$$

(5, 6) Dihydride.



$$\begin{array}{l}Ph{\cdot}C{\cdot}NH{\cdot}CH\\Ph{\cdot}\ddot{C}{\cdot}NH{\cdot}\ddot{C}H\end{array},$$

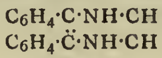
(1, 4) Dihydride.



$$\begin{array}{l}Ph{\cdot}C{\cdot}N{\cdot}CH\\Ph{\cdot}\ddot{C}{\cdot}\dot{N}{\cdot}\ddot{C}H\end{array}.$$

(2, 3) Diphenylpiazine.

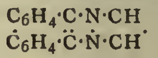
By the interaction of phenanthraquinone and ethylenediamine, only two compounds are obtained, neither of which, however, is re-converted into its generators by chlorhydric acid; they are represented by the formulæ—



$$\begin{array}{l}C_6H_4{\cdot}C{\cdot}NH{\cdot}CH\\C_6H_4{\cdot}\ddot{C}{\cdot}NH{\cdot}CH\end{array}$$

Phenanthrapiazine (1, 4) dihydride.

and



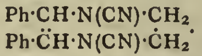
$$\begin{array}{l}C_6H_4{\cdot}C{\cdot}N{\cdot}CH\\\dot{C}_6H_4{\cdot}\ddot{C}{\cdot}\dot{N}{\cdot}CH\end{array}.$$

Phenanthrapiazine.

A series of analogous compounds prepared from other ketones of the phenanthrene (retene and chrysene quinones) series and ethylene- and propylene-diamine are described; their general properties are shown to be similar to those of phenanthrapiazine (1, 4) dihydride and phenanthrapiazine.

50. "*Piazine Derivatives.*" (III.) By Arthur T. Mason, Ph.D., and L. A. Dryfoos, Ph.D.

Details are given of the mode of preparing (2, 3) diphenylpiazine (1, 4) dihydride and of its dibenzoyl and its diacetyl derivatives. An addition product obtained by the interaction of the (5, 6) dihydride and hydrogen cyanide in alcoholic solution is described; as this is converted into diphenylpiazine by alcoholic potash, it is to be supposed that the cyanogen radicles are attached to the nitrogen atoms. The constitutional formula of the compound is very probably—



$$\begin{array}{l}Ph{\cdot}CH{\cdot}N(CN){\cdot}CH_2\\Ph{\cdot}\ddot{C}H{\cdot}N(CN){\cdot}\dot{C}H_2\end{array}.$$

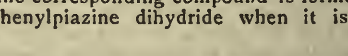
An account is given of a new method of preparing (2, 3) diphenylpiazine, which consists in heating the (5, 6) dihydride with alcoholic potash; a small quantity of a complicated compound—tetraphenyldipiazine—is also formed, which is distinguished by its sparing solubility in the ordinary solvents.

The products of the interaction of dimethoxybenzil or anisil and ethylenediamine, viz., (2, 3) dimethoxyphenylpiazine (5, 6) dihydride and (2, 3) dimethoxyphenylpiazine, are described.

It is shown that, when submitted to the action of potassium cyanide, (2, 3) diphenylpiazine (5, 6) dihydride yields the amide of (2, 3) diphenylpiazinecarboxylic acid, and that the corresponding compound is formed from dimethoxyphenylpiazine dihydride when it is similarly treated.

51. "*Condensation Products from Ethylenediamine and Derivatives of Acetoacetic Acid.*" (IV.). By Arthur T. Mason, Ph.D., and L. A. Dryfoos, Ph.D.

The authors describe ethylic ethylene-β-amidomethylcrotonate,—



$$\begin{array}{l}CH_3{\cdot}C{\cdot}NH{\cdot}C_2{\cdot}H_4{\cdot}NH{\cdot}C{\cdot}CH_3\\\quad\ \ \ddot{C}Et{\cdot}CO_2Et\qquad\quad \ddot{C}Et{\cdot}CO_2Et\end{array},$$

obtained by the interaction of ethylic methylacetoacetate and ethylenediamine; and also the corresponding compounds from ethylic ethylacetoacetate and methylic acetoacetate.

52. "*Studies of the Oxidation Products of Turpentine.*" By S. B. Schryver, Ph.D., B.Sc.

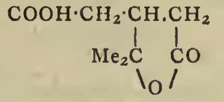
The author finds that on oxidising turpentine with chromic mixture, besides terebic and terpenylic acids, a third acid is obtained having the same composition as camphoronic acid, $C_9H_{14}O_6$, but differing from it in electric conductivity (0·0102 instead of 0·0175): it is contained in the mother-liquors from which the other acids have been separated, and is isolated through the agency of an insoluble lead salt. The crude acid fused at 125—160°, but after repeated crystallisation from nitric acid at 135—137°.

With the object of determining the constitution of terpenylic acid, attempts were made to synthesise various heptolactones; eventually that prepared from the methylisopropyllactic acid of the formula—

$$PrCMe(OH){\cdot}CH_2{\cdot}COOH$$

was found to be identical with the lactone prepared from teracrylic acid.

On reducing terpenylic acid with iodhydric acid an acid was obtained which is shown to be identical with $\beta$-isopropylglutaric acid prepared synthetically by condensing isobutaldehyde and ethylic malonate, combining the product with ethylic sodiomalonate, and hydrolysing the resulting tetrethylic salt. The conclusion is arrived at that terpenylic acid is to be represented by the formula—



53. "*Addendum to Note on the Nature of Depolarisers.*" By Henry E. Armstrong.

I am induced to somewhat extend my recent note on depolarisers in order that the argument there made use of in considering the dissolution of metals such as magnesium in nitric acid may be clearly understood and its consequences more fully realised.

It is one of the most noteworthy features of such interactions that when reduction is carried beyond the nitric oxide stage, it invariably proceeds to ammonia, and gives rise to a variety of products; so that whereas neither nitrous oxide nor nitrogen is evolved when metals such as silver and mercury are dissolved, these two gases are always obtained when more active metals are the agents. From this it would appear that there is a limit of (?) electromotive force which must be exceeded if it be desired to extend the reduction beyond the stage involving the formation merely of nitrogen dioxide and monoxide.

A somewhat similar case is presented by the behaviour of sulphuric acid solutions on electrolysis. Whereas, besides hydrogen, only oxygen is obtained under certain conditions, under others ozone, persulphuric acid, and hydrogen peroxide are also produced. This apparently is a phenomenon of the same order, but in a measure the converse of that presented by nitric acid, as oxygen—not hydrogen—is the active substance. Judging from McLeod's observations (*C. S. Trans.*, 1886, 591), it is clear that "current density" is an all-important factor in determining "peroxidation," but it remains to be determined whether it is the sole factor: the individual influence of electromotive force, of current strength, and of current density, in fact, all require careful study in this as in many other cases of electrolysis; undoubtedly much depends on the concentration of the acid. The peroxidation may be regarded as the outcome of oxygen depolarisation, effected apparently in two ways: part of the oxygen becoming affixed to sulphuric acid, persulphuric acid is formed, which in part gradually undergoes hydrolysis, affording hydrogen peroxide—a non-electrolytic change; while another part serves as oxygen depolariser, affording ozone. On this assumption, ozone is not the product of the fortuitous concourse of three oxygen atoms, but of the interaction of oxygen atoms in circuit with persulphuric acid; and if this be the origin of electrolytic ozone, it appears not improbable that the oxidation of phosphorus, which is attended by the formation of ozone, will also be found to involve the formation of a peroxide hitherto undiscovered.

In the case of a metal such as magnesium dissolving in considerable excess of nitric acid, if a plate be imagined to be undergoing attack and conversion into nitrate at any one point, the displaced hydrogen may, it would seem, "travel along" a very large number of paths to other points on the plate capable of acting as negative pole and of there meeting with nitric acid in sufficient amount to oxidise it, and it is scarcely conceivable, therefore, that it should escape if the nitric acid act directly as depolariser. It is also difficult to understand why one substance, an electrolyte, should act in two ways in the same circuit, and the difficulty appears to be equally great whether any form of Grothus' hypothesis, or a dissociation hypothesis, be adopted in explanation of electrolysis. But these difficulties seemingly disappear if—as previously suggested—the active depolariser be a nitrous compound or derivative; perhaps, at all events, at the initial stage, nitrogen dioxide. Moreover, it would appear to be possible in this manner to account also for the extension of the reduction to ammonia: in the case of a metal like silver the amount of depolariser must always tend to reach a maximum value depending on the extent to which the reversible interchange expressed by the equation $NO+2HNO_3=3NO_2+OH_2$ is limited by the concentration and temperature; but it is limited by these conditions alone. In the case of more active metals, it appears probable that the nitric oxide also functions as depolariser and is reduced to hydroxylamine and ultimately to ammonia. If such an action take place, it follows (from Ohm's law) that the more active the metal the more rapidly will hydrogen be displaced by it, giving greater opportunity therefore for nitric oxide to undergo reduction and leading to the production of an increased proportion of products of extended reduction. Any circumstance which would tend to diminish the proportion of nitrogen dioxide relatively to monoxide present in solution would, therefore, promote the formation of such products, and, in point of fact, Acworth and I have noticed, even in the case of copper, that when the metal is dissolved in diluted nitric acid, it appears to be more "active," *i.e.*, to furnish a larger proportion of products of extended reduction, than when more concentrated acid is used: as the presence of water must obviously favour the reversal of the interchange expressed by the equation $NO+2HNO_3=3NO_2+H_2O$, so that weaker would potentially contain a larger proportion of monoxide than stronger solutions of nitric acid, these observations would appear to be in harmony with the hypothesis here advocated. There is no evidence, be it remarked, that hyponitrous acid can be formed in acid solution, *i.e.*, by direct reduction of nitric or even of nitrous acid, and the whole of the nitrous oxide which is evolved when metals are dissolved in nitric acid may result from the interaction of nitrous acid and hydroxylamine. That reduction invariably extends to ammonia whenever hydroxylamine is formed is probably a consequence of the extreme readiness with which hydroxylamine is itself reduced; so that, in fact, when reduction once proceeds beyond the nitric oxide stage, it is to be supposed that there are necessarily a number of competing depolarisers present in solution—nitrogen dioxide and monoxide and hydroxylamine (and perhaps others), none of which, however, are electrolytes in the sense in which the term is ordinarily understood. And here it may be pointed out that the fact that a nitrate may be reduced in alkaline solution by sodium amalgam, or aluminium, or zinc, is no argument against the conclusion above arrived at that probably nitric acid does not directly act as depolariser, as in these cases the alkaline solution appears to be the electrolyte and the nitrate merely the depolariser—so that the nitrate does not act in two ways. As nitrates may be wholly converted into ammonia by reducing an alkaline solution, it would seem probable that in such cases hydroxylamine is not an intermediate product, as nitrogen is obtained on boiling an alkaline solution of this substance.

The argument here made use of would appear also to afford an explanation of the effect produced by varying the electromotive force, *i.e.*, by metals of different degrees of "activity": as increase of electromotive force, other conditions remaining unchanged, would increase the current strength, and consequently the rate of change; and, as indicated above, an increase in the rate of change would doubtless involve an increase in the amount of products of extended reduction.

It remains to be pointed out that the objection made to the assumption that nitric acid can act in two ways is equally applicable to the case of sulphuric acid; in other words, that it is not likely that sulphuric acid would act as electrolyte and as oxygen depolariser. It becomes necessary, therefore, to reconsider the manner in which solutions of this acid undergo electrolysis. On the one hand it is conceivable that the water molecule alone suffers partition, not the sulphuric acid ($H_2SO_4$) molecule, as commonly supposed, and that under certain conditions the latter takes a direct part in the change, becoming oxidised; but this does not appear to be probable, especially as there is reason to believe that the acid in conjunction with water actually functions as electrolyte. An alternative assumption would be that the immediate product has been overlooked, and it can scarcely be gainsaid that there is much evidence in favour of this view. It is not improbable that the first products of electrolysis are hydrogen and *persulphuric* acid; it may be supposed that under "ordinary" circumstances this latter substance is resolved at the electrode surface into oxygen and sulphuric acid, but when the electrode surface is small much escapes unchanged, this being especially the case when the electrolyte is a somewhat concentrated acid—a condition which in itself favours the survival of persulphuric acid. Not only do recent observations on the electrolysis of various sulphates support this contention, but it would seemingly also serve to explain the extraordinary character of the curve representing the change in conductivity of solutions of sulphuric acid on dilution.

54. "*The Molecular Complexity of Liquids.*" By William Ramsay, Ph.D., F.R.S., and John Shields, Ph.D., D.Sc.

From the ascent of a liquid in a capillary tube of known diameter and its relative density, the surface tension of the liquid may be calculated. The molecular volume of a liquid, at any temperature, is proportional to the number of molecules contained in unit volume at that temperature; and the two-thirds root of the number representing the molecular volume is proportional to the number of molecules distributed in unit surface, with the proviso that the mean distance between 2 mols. at the surface is equal to that between any 2 mols. in the interior. Multiplying the number representing surface tension by that representing molecular surface, the product may be termed "molecular surface energy." By stating surface tension in degrees, and molecular surface in square centimetres, the product is expressed in ergs, and may be defined as the work required to produce or to extend a surface on which equal numbers of molecules lie.

This energy is *nil* at the critical temperature of the liquid, for there is no surface. It increases with fall of temperature, and after about 20° below the critical temperature, the rate of increase is practically a linear function of the temperature. The equation which exhibits this relation is—

$$\gamma(Mv)^{\frac{2}{3}}=k(\tau-d),$$

where the letters have the following definitions:—

$\gamma$, surface tension,
M, molecular weight,
$v$, specific volume,
$k$, a numerical constant,
$\tau$, temperature measured downwards from the critical temperature,
$d$, being a numerical constant equal to about 6.

This equation is analogous to that which expresses volume energy in its relation to heat, viz., $pv=RT$.

As a gas is said to be normal if, when $v$ expresses the volume of its molecular weight taken in grms., and $p$ is measured in atmospheres, R is constant between various limits of temperature, so a liquid may be said to be normal, *i.e.*, to be composed of molecules of no greater degree of complexity than those which form its gas, if the value of $k$ is constant between various limits of temperature. This affords a means, therefore of investigating the molecular weights of liquids as such, and it is the first colligative property of liquids which has been discovered.

In all fifty-seven liquids have been investigated. They divide themselves into two groups: those of which the molecules are simple (thirty six in number), and those which, in the liquid state, consist of molecules composed of several gaseous molecules coalesced to form a complex. To the latter class belong the alcohols, the acids, water, phenol, and three others, nitroethane, acetonitrile, and acetone.

It is remarkable that, so far as our experiments have gone, no liquid shows a greater molecular complexity than that in which the molecular weight of the gas is multiplied by the factor 4. Water at 0° has approximately the formula $H_8O_4$, *i.e.*, $(H_2O)_4$; the degree of complexity, however, is altered by rise of temperature, and the complex molecules gradually dissociate into more simple groups.

A determination of molecular surface energy also permits of a close estimate of the critical temperatures of "normal" liquids. The numbers representing these important data are given in the complete memoir.

55. "*The Preparation of Active Amyl Alcohol and Active Valeric Acid from Fusel Oil.*" By W. A. C. Rogers.

The author has prepared the alcohol by a modification of Le Bel's method communicated to him by Professor Odling and Mr. Marsh, which consists in heating the alcohol with a fuming aqueous solution of hydrogen chloride in closed tubes at 100°, the treatment being repeated until the rotatory power of the product reached a maximum. Finally, from 16·2 litres of purified fusel oil, he obtained 250 c.c. of an alcohol rotating $-8°\,30'$ per 200 m.m. at 22° (or $[\alpha]_D=-5{\cdot}2°$). By oxidising this alcohol, a valeric acid was obtained rotating 26° per 200 m.m. at 22° ($[\alpha]_D=13{\cdot}9°$). The values thus obtained are practically identical with those given by Guye and Chavanne in a recent paper.

*Research Fund.*

A donation of £100 to the Research Fund has been received from Mr. L. Mond, F.R.S., by the Treasurer since the meeting of the Society.

## CORRESPONDENCE.

### SODIUM PEROXIDE.

*To the Editor of the Chemical News.*

Sir,—I notice in the *Transactions of the Chemical Society* for September, 1893, a paper by Dr. J. Clark on the "Use of Sodium Peroxide as an Analytical Agent." I think it only fair to myself to state that the usefulness of this substance as a reagent in analysis and as a source of hydrogen peroxide occurred to me nearly two years ago, and I suggested its use to Mr. Alfred Allen, F.I.C., &c., in a letter dated October, 1891, that is, prior to the patent of the Aluminium Company, and therefore before this substance had attracted my attention. I made some experiments with the substance, but not on a very extended scale, and not in any way comparable in point of thoroughness with those described in Dr. Clark's paper, which I have no desire to undervalue. I found it difficult to make solutions of hydrogen peroxide of greater than one-volume strength without great loss of oxygen, and as my idea was to use the sodium peroxide to make solutions of hydrogen peroxide, this militated against its apparent chance of success. I noticed its power of converting manganese salts into the green manganate, and suggested its use to Mr. Allen for oxidising sulphuretted hydrogen into sulphuric acid in the well-known estimation of sulphur in steel by evolution of sulphuretted hydrogen.

On looking through the literature of the subject I found only two papers, viz., the original paper by Davy and an exhaustive one by Vernon Harcourt (*Chem. Soc. Journ.*, xiv., 276). There was also a paper by Fairley (*Chem. Soc. Journ.*, 1877, i., 125), in which hydrated peroxides are produced by adding hydrogen peroxide to caustic soda in alcoholic solution.

No doubt Mr. Allen will be able to corroborate the statements with which I have associated his name.—I am, &c.,

H. K. Tompkins.

Gipsy Hill, London, S.W.,
September 7, 1893.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 9, August 28, 1893.

This issue contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., No. 12.

**Titration of Morphine in Opium.**—Cannepin and Van Eyk.—The author operates as follows:—He weighs 10 grms. of opium, 4 grms. of slaked lime, and grinds them carefully in a mortar, adding by portions 100 c.c. of the solution of morphine hydrochlorate indicated (0·805 grm. per litre), and digests for half an hour, stirring from time to time. He throws the mixture upon a filter, and evaporates rapidly the 20 c.c. filtrate upon a water-bath at 100°. He weighs off of the filtrate a weight equal to 50 grms. plus the weight of the fixed soluble matters yielded by 5 grms. of opium, which makes about 52 grms. He adds to the liquid 10 c.c. of ether, and agitates so as to saturate the aqueous solution. He adds further one-half grm. ammonium hydrochlorate (free from carbonate), agitates until the precipitate appears, and allows to settle for two hours. He decants the ether and throws it upon a tared filter, through which all the liquid is filtered. The precipitate of morphine is collected, and washed with morphine water (0·42 grm. morphine per litre) until the filter and the precipitate are decolourised. The filter and its contents are then dried in the stove at a temperature not exceeding 98° and weighed. The solution of morphine hydrochlorate indicated contains 0·805 grm. of crystalline morphine hydrochlorate per litre. The author adds it to compensate an error.

**A New Method for the Detection of Alkaloids, Saccharine, and Salicylic Acid.**—MM. Lindeman and Motten.—This paper will be inserted in full.

**Volumetric Determination of Pyrophosphoric Acid and the Alkaline Pyrophosphates.**—G. Farrel.—The author adds to the solution of pyrophosphate a tincture of cochineal, and runs into the mixture decinormal acid until the colour turns to a yellow; each c.c. then represents 0·0089 grm. of pyrophosphoric acid. No free alkali must be present along with the alkaline pyrophosphate. In such a case the free alkali is first determined, using soluble blue as indicator. A second determination is then made, using cochineal as an indicator. The difference in the number of c.c. used in the second and first titration, multiplied by 0·0089, will give the pyrophosphoric acid. If there is an alkaline carbonate in presence of the pyrophosphate, the author first determines the total alkali, using cochineal; in an equal volume of the liquid he adds the same number of c.c. of decinormal acid as that employed in the first operation, and then decinormal soda until the colour turns in presence of soluble blue. The number of c.c. used multiplied by 0·0089 will again give the quantity of pyrophosphoric acid. The author's results authorised him to conclude that pyrophosphoric acid is monobasic in presence of cochineal, but bibasic with soluble blue (Poirrier's $C_4B$) if we operate at the ordinary temperature.

**Volumetric Determination of Alkalies in Alkaline Arsenites.**—G. Farrel.—The author has studied the action of alkalies with arsenious acid in presence of some indicators. He first prepared a solution of 1-10th equiv. arsenious acid (9·9 grms.) in 2-10ths equiv. of soda (6·2 grms.) so as to obtain a litre of liquid with distilled water. If to 10 c.c. of this decinormal solution we add 20 c.c. of decinormal acid, all the alkali is saturated, the liquid remaining clear and the arsenious acid subsiding only after a very long time. The 10 c.c. of arsenious acid thus set at liberty, after the addition of a few drops of tincture of cochineal, always require for the change of colour one or at most two drops of decinormal soda; arsenious acid seems therefore indifferent to cochineal. In presence of phthalein it is necessary under the same conditions to add 2 to 3 c.c. of decinormal soda to effect the change; with soluble blue ($C_4B$ Poirrier) we have to use 12 or 13 c.c. Hence it results that if to a solution of an alkaline arsenite we add decinormal acid and a few drops of tincture of cochineal, the alkalinity will remain as long as we do not add a quantity of acid equivalent to that of the base combined with the arsenious acid. Hence we can easily determine the alkali in arsenites if we use exclusively cochineal as the indicator. It will not be the same if we use phenolphthalein or soluble blue. We determine, in the ordinary manner, the arsenious acid by means of decinormal iodine (Mohr's method), and the alkali combined with it by means of a decinormal acid with cochineal as the indicator.

**Amidonaphtholsulphonic Acids.**—F. Reverdin and Ch. de la Harpe.—This lengthy memoir does not admit of convenient abstraction.

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Nottingham, 1893.

## INAUGURAL ADDRESS OF THE PRESIDENT,

J. C. Burdon-Sanderson, M.A., M.D., LL.D., D.C.L., F.R.S., F.R.S.E.,
Professor of Physiology in the University of Oxford.

(Concluded from p. 131.)

### *The Specific Energies of the Organism.*

When in 1826 J. Müller was engaged in investigating the physiology of vision and hearing he introduced into the discussion a term "specific energy," the use of which by Helmholtz[*] in his physiological writings has rendered it familiar to all students. Both writers mean by the word energy, not the "capacity of doing work," but simply *activity*, using it in its old-fashioned meaning, that of the Greek word from which it is derived. With the qualification "specific" it serves, perhaps, better than any other expression to indicate the way in which adaptation manifests itself. In this more extended sense the "specific energy" of a part or organ—whether that part be a secreting cell, a motor cell of the brain or spinal cord, or one of the photogenous cells which produce the light of the glow-worm, or the protoplasmic plate which generates the discharge of the torpedo—is simply the special action which it *normally* performs, its norma or rule of action being in each instance the *interest of the organism* as a whole of which it forms part, and the exciting cause some influence outside of the excited structure, technically called a stimulus. It thus stands for a characteristic of living structures which seem to be universal. The apparent exceptions are to be found in those bodily activities which, following Bichat, we call vegetative, because they go on, so to speak, as a matter of course; but the more closely we look into them the more does it appear that they form no exception to the general rule, that every link in the chain of living action, however uniform that action may be, is a response to an antecedent influence. Nor can it well be doubted that, as every living cell or tissue is called upon to act in the interest of the whole, the organism must be capable of influencing every part so as to regulate its action. For, although there are some instances in which the channels of this influence are as yet unknown, the tendency of recent investigations has been to diminish the number of such instances. In general there is no difficulty in determining both the nature of the central influence exercised, and the relation between it and the normal function. It may help to illustrate this relation to refer to the expressive word *Auslösung* by which it has for many years been designated by German writers. This word stands for the performance of function by the "letting off" of "specific energies." Carrying out the notion of "letting off" as expressing the link between action and reaction, we might compare the whole process to the mode of working of a repeating clock (or other similar mechanism), in which case the pressure of the finger on the button would represent the external influence or stimulus, the striking of the clock the normal reaction. And now may I ask you to consider in detail one or two illustrations of physiological reaction—of the *letting off of specific energy?*

The repeater may serve as a good example, inasmuch as it is, in biological language, a highly differentiated structure, to which a single function is assigned. So also in the living organism, we find the best examples of specific energy where Müller found them, namely, in the most differentiated, or, as we are apt to call them, the *highest* structures. The retina, with the part of the brain which belongs to it, together constitute such a structure, and will afford us therefore the illustration we want, with this advantage for our present purpose, that the phenomena are such as we all have it in our power to observe in ourselves. In the visual apparatus the principle of *normality* of reaction is fully exemplified. In the physical sense the word "light" stands for ether vibrations, but in the sensuous or subjective sense for sensations. The swings are the stimulus, the sensations are the reaction. Between the two comes the link, the "letting off," which it is our business to understand. Here let us remember that the man who first recognised this distinction between the physical and the physiological was not a biologist, but a physicist. It was Young who first made clear (though his doctrine fell on unappreciative ears) that, although in vision the external influences which give rise to the sensation of light are infinitely varied, the responses need not be more than three in number, each being, in Müller's language, a "specific energy" of some part of the visual apparatus. We speak of the organ of vision as *highly differentiated*, an expression which carries with it the suggestion of a distinction of rank between different vital processes. The suggestion is a true one; for it would be possible to arrange all those parts or organs of which the bodies of the *higher* animals consist in a series, placing at the lower end of the series those of which the functions are continuous, and therefore called vegetative; at the other, those highly specialised structures, as, *e.g.*, those in the brain, which in response to physical light produce physiological, that is subjective, light; or, to take another instance, the so-called motor cells of the surface of the brain, which, in response to a stimulus of much greater complexity, produce voluntary motion. And just as in civilised society an individual is valued according to his power of doing one thing well, so the high rank which is assigned to the structure, or rather to the "specific energy" which it represents, belong to it by virtue of its specialisation. And if it be asked how this conformity is manifested, the answer is, by the quality, intensity, duration, and extension of the response, in all which respects vision serves as so good an example, that we can readily understand how it happened that it was in this field that the relation between response and stimulus was first clearly recognised. I need scarcely say that, however interesting it might be to follow out the lines of inquiry thus indicated, we cannot attempt it this evening. All that I can do is to mention one or two recent observations which, while they serve as illustrations, may perhaps be sufficiently novel to interest even those who are at home in the subject.

Probably everyone is acquainted with some of the familiar proofs that an object is seen for a much longer period than it is actually exposed to view; that the visual reaction lasts much longer than its cause. More precise observations teach us that this response is regulated according to laws which it has in common with all the higher functions of an organism. If, for example, the cells in the brain of the torpedo are "let off"—that is, awakened by an external stimulus—the electrical discharge, which, as in the case of vision, follows after a certain interval, lasts a certain time, first rapidly increasing to a maximum of intensity, then more slowly diminishing. In like manner, as regards the visual apparatus, we have, in the response to a sudden invasion of the eye by light, a rise and fall of a similar character. In the case of the electrical organ, and in many analogous instances, it is

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[*] "Handb. der Physiologischen Optik," 1886, p. 233. Helmholtz uses the word in the plural—the "energies of the nerves of special sense."

easy to investigate the time relations of the successive phenomena, so as to represent them graphically. Again, it is found that in many physiological reactions, the period of rising "energy" (as Helmholtz called it) is followed by a period during which the responding structure is not only inactive, but its capacity for energising is so completely lost that the same exciting cause which a moment before "let off" the characteristic response is now without effect. As regards vision, it has long been believed that these general characteristics of physiological reaction have their counterpart in the visual process, the most striking evidence being that in the contemplation of a lightning flash — or, better, of an instantaneously illuminated white disc*—the eye seems to receive a double stroke, indicating that, although the stimulus is single and instantaneous, the response is reduplicated. The most precise of the methods we until lately possessed for investigating the wax and wane of the visual reaction, were not only difficult to carry out but left a large margin of uncertainty. It was therefore particularly satisfactory when M. Charpentier, of Nancy, whose merits as an investigator are perhaps less known than they deserve to be, devised an experiment of extreme simplicity which enables us, not only to observe, but to measure with great facility both phases of the reaction. It is difficult to explain even the simplest apparatus without diagrams; you will, however, understand the experiment if you will imagine that you are contemplating a disc, like those ordinarily used for colour mixing; that it is divided by two radial lines which diverge from each other at an angle of 60°; that the sector which these lines enclose is white, the rest black; that the disc revolves slowly, about once in two seconds. You then see, close to the front edge of the advancing sector, a black bar, followed by a second at the same distance from itself but much fainter. Now the scientific value of the experiment consists in this, that the angular distance of the bar from the black border is in proportion to the frequency of the revolutions —the faster, the wider. If, for example, when the disc makes half a revolution in a second the distance is ten degrees, this obviously means that when light bursts into the eye, the extinction happens one-eighteenth of a second after the excitation.†

The fact thus demonstrated, that the visual reaction, consequent on an instantaneous illumination, exhibits the alterations I have described, has enabled M. Charpentier to make out another fact in relation to the visual reaction which is, I think, of equal importance. In all the instances, excepting the retina, in which the physiological response to stimulus has a definite time-limitation, and in so far resembles an explosion—in other words, in all the higher forms of specific energy—it can be shown experimentally that the process is propagated from the part first directly acted on to other contiguous parts of similar endowment. Thus in the simplest of all known phenomena of this kind, the electrical change, by which the leaf of the Dionæa plant responds to the slightest touch of its sensitive hairs, is propagated from one side of the leaf to the other, so that in the opposite lobe the response occurs after a delay which is proportional to the distance between the spot excited and the spot observed. That in the retina there is also such propagation has not only been surmised from analogy, but inferred from certain observed facts. M. Charpentier has now been able by a method which, although simple, I must not attempt to describe, not only to prove its existence, but to measure its rate of progress over the visual field.

There is another aspect of the visual response to the stimulus of light which, if I am not trespassing too long on your patience, may, I think, be interesting to consider. As the relations between the sensations of colour and the physical properties of the light which excites them, are among the most certain and invariable in the whole range of vital reactions, it is obvious that they afford as fruitful a field for physiological investigation as those in which white light is concerned. We have on one side physical facts, that is, wave-lengths or vibration-rates; on the other, facts in consciousness—namely, sensations of colour—so simple that notwithstanding their subjective character there is no difficulty in measuring either their intensity or their duration. Between these there are *lines of influence*, neither physical nor psychological, which pass from the former to the latter through the visual apparatus (retina, nerve, brain). It is these lines of influence which interest the physiologist. The structure of the visual apparatus affords us no clues to trace them by. The most important fact we know about them is that they must be at least three in number.

It has been lately assumed by some that vision, like every other specific energy having been developed progressively, objects were seen by the most elementary forms of eye only in chiaroscuro, that afterwards some colours were distinguished, eventually all. As regards hearing it is so. The organ which, on structural grounds, we consider to represent that of hearing in animals low in the scale of organisation—as, *e.g.*, in the Ctenophora—has nothing to do with sound,* but confers on its possessor the power of judging of the direction of its own movements in the water in which it swims, and of guiding these movements accordingly. In the lowest vertebrates, as, *e.g.*, in the dogfish, although the auditory apparatus is much more complicated in structure, and plainly corresponds with our own, we still find the particular part which is concerned in hearing scarcely traceable. All that is provided for is that sixth sense, which the higher animals also possess, and which enables them to judge of the direction of their own movements. But a stage higher in the vertebrate series we find the special mechanism by which we ourselves appreciate sounds beginning to appear—not supplanting or taking the place of the imperfect organ, but added to it. As regards hearing, therefore, a new function is acquired without any transformation or fusion of the old into it. We ourselves possess the sixth sense, by which we keep our balance and which serves as the guide to our bodily movements. It resides in the part of the internal ear which is called the labyrinth. At the same time we enjoy along with it the possession of the cochlea, that more complicated apparatus by which we are able to hear sounds and to discriminate their vibration rates.

As regards vision, evidence of this kind is wanting. There is, so far as I know, no proof that visual organs which are so imperfect as to be incapable of distinguishing the forms of objects, may not be affected differently by their colours. Even if it could be shown that the least perfect forms of eye possess only the power of discriminating between light and darkness, the question whether in our own such a faculty exists separately from that of distinguishing colours is one which can only be settled by experiment. As in all sensations of colour the sensation of brightness is mixed, it is obvious that one of the first points to be determined is whether the latter represents a "specific energy" or merely a certain combination of specific energies which are excited by colours. The question is not whether there is such a thing as white light, but whether we possess a separate faculty by which we judge of light and shade—a question which, although we have derived our knowledge of it chiefly from physical experiment, is one of eye and brain, not of wave-lengths or vibration-rates, and is therefore essentially physiological.

There is a German proverb which says, "Bei Nacht

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[*] The phenomenon is best seen when, in a dark room, the light of a luminous spark is thrown on to a white screen with the aid of a suitable lens.

[†] Charpentier, "Réaction oscillatoire de la Rétine sous l'influence des excitations lumineuses," *Archives der Physiol.*, vol. xxiv., p. 541; and "Propagation de l'action oscillatoire, &c.," p. 362.

[*] Verworn, "Gleichgewicht u. Otolithenorgan," *Pflüger's Archiv.*, vol. l., p. 423; also Ewald's "Researches on the Labyrinth as a Sense-organ" ("Ueber das Endorgan des Nervus octavus," Wiesbaden, 1892).

sind alle Katzen grau." The fact which this proverb expresses presents itself experimentally when a spectrum projected on a white surface is watched, while the intensity of the light is gradually diminished. As the colours fade away they become indistinguishable as such, the last seen being the primary red and green.[*] Without entering into details, let us consider what this tells us of the specific energy of the visual apparatus. Whether or not the faculty by which we see grey in the dark is one which we possess in common with animals of imperfectly developed vision, there seems little doubt that there are individuals of our own species, who in the fullest sense of the expression have no eye for colour; in whom all colour sense is absent; persons who inhabit a world of grey, seeing all things as they might have done had they and their ancestors always lived nocturnal lives. In the theory of colour vision, as it is commonly stated, no reference is made to such a faculty as we are now discussing.

Professor Hering, whose observations as to the diminished spectrum I referred to just now, who was among the first to subject the vision of the *totally* colour-blind to accurate examination, is of opinion, on that and on other grounds, that the sensation of light and shade is a specific faculty. Very recently the same view has been advocated on a wide basis by a distinguished psychologist, Professor Ebbinghaus.[†] Happily, as regards the actual experimental results relating to both these main subjects, there seems to be a complete coincidence of observation between observers who interpret them differently. Thus the recent elaborate investigations of Captain Abney[‡] (with General Festing), representing graphically the results of his measurements of the subjective values of the different parts of the diminished spectrum, as well as those of the fully illuminated spectrum as seen by the totally colour-blind, are in the closest accord with the observations of Hering, and have, moreover, been substantially confirmed in both points by the measurements of Dr. König in Helmholtz's laboratory at Berlin.[§] That observers of such eminence as the three persons whom I have mentioned, employing different methods and with a different purpose in view, and without reference to each other's work, should arrive in so complicated an inquiry at coincident results, augurs well for the speedy settlement of this long-debated question. At present the inference seems to be that such a specific energy as Hering's theory of vision postulates actually exists, and that it has for associates the colour-perceiving activities of the visual apparatus, provided that these are present; but that whenever the intensity of the illumination is below the chromatic threshold—that is, too feeble to awaken these activities—or when, as in the totally colour-blind, they are wanting, it manifests itself independently; all of which can be most easily understood on such a hypothesis as has lately been suggested in an ingenious paper by Mrs. Ladd Franklin,[||] that each of the elements of the visual apparatus is made up of a central structure for the sensation of light and darkness, with collateral appendages for the sensations of colour—it being, of course, understood that this is a mere diagrammatic representation, which serves no purpose beyond that of facilitating the conception of the relation between the several "specific energies."

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### *Phototaxis and Chemiotaxis.*

Considering that every organism must have sprung from a unicellular ancestor, some have thought that unless we are prepared to admit a deferred epigenesis of mind, we must look for psychical manifestations even among the lowest animals, and that as in the protozoon all the vital activities are blended together, mind should be present among them not merely potentially but actually, though in diminished degree.

Such a hypothesis involves ultimate questions which it is unnecessary to enter upon: it will, however, be of interest in connection with our present subject to discuss the phenomena which served as a basis for it—those which relate to what may be termed the behaviour of unicellular organisms and of individual cells, in so far as these last are capable of reacting to external influences. The observations which afford us most information are those in which the stimuli employed can be easily measured, such as electrical currents, light, or chemical agents in solution.

A single instance, or at most two, must suffice to illustrate the influence of light in directing the movements of freely-moving cells, or, as it is termed, phototaxis. The rod-like purple organism called by Engelmann *Bacterium photometricum*,[*] is such a light-lover that if you place a drop of water containing these organisms under the microscope, and focus the smallest possible beam of light on a particular spot in the field, the spot acts as a light trap and becomes so crowded with the little rodlets as to acquire a deep port wine colour. If instead of making his trap of white light, he projected on the field a microscopic spectrum, Engelmann found that the rodlets showed their preference for a spectral colour which is absorbed when transmitted through their bodies. By the aid of a light trap of the same kind, the very well-known spindle-shaped and flagellate cell of Euglena can be shown to have a similar power of discriminating colour, but its preference is different. This familiar organism advances with its flagellum forwards, the sharp end of the spindle having a red or orange eye point. Accordingly, the light it loves is again that which is most absorbed—viz., the blue of the spectrum (line F).

These examples may serve as an introduction to a similar one in which the directing cause of movement is not physical but chemical. The spectral light trap is used in the way already described; the organisms to be observed are not coloured, but bacteria of that common sort which twenty years ago we used to call *Bacterium termo*, and which is recognised as the ordinary determining cause of putrefaction. These organisms do not care for light, but are great oxygen-lovers. Consequently, if you illuminate with your spectrum a filament of a confervoid alga, placed in water containing bacteria, the assimilation of carbon and consequent disengagement of oxygen is most active in the part of the filament which receives the red rays (B to C). To this part, therefore, where there is a dark band of absorption, the bacteria which want oxygen are attracted in crowds. The motive which brings them together is their desire for oxygen. Let us compare other instances in which the source of attraction is food.

The plasmodia of the myxomycetes, particularly one which has been recently investigated by Mr. Arthur Lister,[†] may be taken as a typical instance of what may be called the chemical allurement of living protoplasm. In this organism, which in the active state is an expansion of labile living material, the delicacy of the reaction is comparable to that of the sense of smell in those animals in which the olfactory organs are adapted to an aquatic life. Just as, for example, the dogfish is attracted by food which it cannot see, so the plasmodium of *Badhamia* becomes aware, as if it smelled it, of the presence of its food—a particular kind of fungus. I have no diagram to

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[*] Hering, "Untersuch. eines total Farbenblinden," *Pfluger's Arch.*, vol. xlix., 1891, p. 563.

[†] Ebbinghaus, "Theorie des Farbensehens," *Zeit. f. Psychol.*, v., 1893, p. 145.

[‡] Abney and Festing, "Colour Photometry," Part III. *Phil. Trans.*, clxxxiii.A, 1891, p. 513.

[§] König, "Ueber den Helligkeitwerth der Spectralfarben bei verschiedener absoluter Intensität," *Beiträge zur Psychologie, &c.*, "Festschrift zu H. von Helmholtz, 70, Geburtstage," 1891, p. 309.

[||] Christine Ladd Franklin, "Eine neue Theorie der Lichtempfindungen," *Zeit. f. Psychologie*, vol. iv., 1893, p. 211; see also the *Proceedings* of the last Psychological Congress in London, 1892.

[*] Engelmann, "Bacterium Photometricum," *Onderzoek. Physiol. Lab. Utrecht*, vol. vii., p. 200; also "Ueber Licht- u. Farbenperception niederster Organismen," *Pfluger's Arch.*, vol. xxix., p. 387.

[†] Lister, "On the Plasmodium of *Badhamia utricularis*, &c." *Annals of Botany*, No. 5. June, 1888.

explain this, but will ask you to imagine an expansion of living material, quite structureless, spreading itself along a wet surface; that this expansion of transparent material is bounded by an irregular coast-line; and that somewhere near the coast there has been placed a fragment of the material on which the *Badhamia* feeds. The presence of this bit of *Stereum* produces an excitement at the part of the plasmodium next to it. Towards this centre of activity streams of living material converge. Soon the afflux leads to an outgrowth of the plasmodium, which in a few minutes advances towards the desired fragment, envelopes, and incorporates it.

May I give you another example also derived from the physiology of plants? Very shortly after the publication of Engelmann's observations of the attraction of bacteria by oxygen, Pfeffer made the remarkable discovery that the movements of the antherozoids of ferns and of mosses are guided by impressions derived from chemical sources, by the allurement exercised upon them by certain chemical substances in solution—in one of the instances mentioned by sugar, in the other by an organic acid. The method consisted in introducing the substance to be tested, in any required strength, into a minute capillary tube, closed at one end, and placing it under the microscope in water inhabited by antherozoids, which thereupon showed their predilection for the substance, or the contrary, by its effect on their movements. In accordance with the principle followed in experimental psychology, Pfeffer[*] made it his object to determine, not the relative effects of different doses, but the smallest perceptible increase of dose which the organism was able to detect; with this result,—that, just as in measurements of the relation between stimulus and reaction in ourselves we find that the sensational value of a stimulus depends, not on its absolute intensity, but on the ratio between that intensity and the previous excitation, so in this simplest of vital reagents the same so-called psycho-physical law manifests itself. It is not, however, with a view to this interesting relation that I have referred to Pfeffer's discovery, but because it serves as a centre around which other phenomena, observed alike in plants and animals, have been grouped. As a general designation of reactions of this kind Pfeffer devised the term Chemotaxis, or, as we in England prefer to call it, Chemiotaxis. Pfeffer's contrivance for chemiotactic testing was borrowed from the pathologists, who have long used it for the purpose of determining the relation between a great variety of chemical compounds or products, and the colourless corpuscles of the blood. I need, I am sure, make no apology for referring to a question which, although purely pathological, is of very great biological interest—the theory of the process by which, not only in man, but also, as Metschnikoff has strikingly shown, in animals far down in the scale of development, the organism protects itself against such harmful things as, whether particulate or not, are able to penetrate its framework. Since Cohnheim's great discovery in 1867 we have known that the central phenomenon of what is termed by pathologists *inflammation* is what would now be called a chemiotactic one; for it consists in the gathering together, like that of vultures to a carcase, of those migratory cells which have their home in the blood stream and in the lymphatic system, to any point where the living tissue of the body has been injured or damaged, as if the products of disintegration which are set free where such damage occurs were attractive to them.

The fact of chemiotaxis, therefore, as a constituent phenomenon in the process of inflammation, was familiar in pathology long before it was understood. Cohnheim himself attributed it to changes in the channels along which the cells moved, and this explanation was generally accepted, though some writers, at all events, recognised its incompleteness. But no sooner was Pfeffer's discovery known than Leber,[*] who for years had been working at the subject from the pathological side, at once saw that the two processes were of similar nature. Then followed a variety of researches of great interest, by which the importance of chemiotaxis in relation to the destruction of disease-producing microphytes was proved, by that of Buchner[†] on the chemical excitability of leucocytes being among the most important. Much discussion has taken place, as many present are aware, as to the kind of wandering cells, or leucocytes, which in the first instance attack morbific microbes, and how they deal with them. The question is not by any means decided. It has, however, I venture to think, been conclusively shown that the process of destruction is a chemical one, that the destructive agent has its source in the chemiotactic cells—that is, cells which act under the orders of chemical stimuli. Two Cambridge observers, Messrs. Kanthack and Hardy,[‡] have lately shown that, in the particular instance which they have investigated, the cells which are most directly concerned in the destruction of morbific *bacilli*, although chemiotactic, do not possess the power of incorporating either bacilli or particles of any other kind. While, therefore, we must regard the relation between the process of devitalising and that of incorporating as not yet sufficiently determined, it is now no longer possible to regard the latter as essential to the former.

There seems, therefore, to be very little doubt that chemiotactic cells are among the agents by which the human or animal organism protects itself against infection. There are, however, many questions connected with this action which have not yet been answered. The first of these are chemical ones—that of the nature of the attractive substance and that of the process by which the living carriers of infection are destroyed. Another point to be determined is how far the process admits of adaptation to the particular infection which is present in each case, and to the state of liability or immunity of the infected individual. The subject is therefore of great complication. None of the points I have suggested can be settled by experiments in glass tubes such as I have described to you. These serve only as indications of the course to be followed in much more complicated and difficult investigations—when we have to do with acute diseases as they actually affect ourselves or animals of similar liabilities to ourselves, and find ourselves face to face with the question of their causes.

It is possibe that many members of the Association are not aware of the unfavourable—I will not say discreditable—position that this country at present occupies in relation to the scientific study of this great subject—the causes and mode of prevention of infectious diseases. As regards administrative efficiency in matters relating to public health, England was at one time far ahead of all other countries, and still retains its superiority; but as regards scientific knowledge we are, in this subject as in others, content to borrow from our neighbours. Those who desire either to learn the methods of research or to carry out scientific inquiries have to go to Berlin, to Munich, to Breslau, or to the Pasteur Institute in Paris, to obtain what England ought long ago to have provided. For to us, from the spread of our race all over the world, the prevention of acute infectious diseases is more important than to any other nation. At the beginning of this address I urged the claims of pure science. If I could, I should feel inclined to speak even more strongly of the application of science to the discovery of the causes of acute diseases. May I express the hope that the effort which is now being made to establish in England an

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[*] Pfeffer, *Untersuch a. d. botan. Institute z. Tübingen*, vol. i. part 3, 1884.

[*] Leber, "Die Anhäufung der Leucocyten am Orte des Entzündungsreizes," &c, *Die Entstehung der Enztundung*," &c., pp. 423—464, Leipzig, 1891.

[†] Buchner, "Die Chem. Reizbarkeit der Leucocyten," &c., *Berliner klin. Woch*, 1890, No. 17.

[‡] Kanthack and Hardy, "On the Characters and Behaviour of the Wandering Cells of the Frog," *Proceedings of the Royal Society*, vol. lii., p. 267.

Institution for this purpose not inferior in inefficiency to those of other countries may have the sympathy of all present? And now may I ask your attention for a few moments more to the subject that more immediately concerns us?

### *Conclusion.*

The purpose which I have had in view has been to show that there is one principle—that of adaptation—which separates biology from the exact sciences, and that in the vast field of biological inquiry the end we have is not merely, as in natural philosophy, to investigate the relation between a phenomenon and the antecedent and concomitant conditions on which it depends, but to possess this knowledge in constant reference to the interest of the organism. It may perhaps be thought that this way of putting it is too teleological, and that in taking, as it were, as my text this evening so old-fashioned a biologist as Treviranus, I am yielding to a retrogressive tendency. It is not so. What I have desired to insist on is that *organism* is a fact which encounters the biologist at every step in his investigations; that in referring it to any general biological principle, such as adaptation, we are only referring it to itself, not explaining it; that no explanation will be attainable until the conditions of its coming into existence can be subjected to experimental investigation so as to correlate them with those of processes in the non-living world.

Those who were present at the meeting of the British Association at Liverpool will remember that then, as well as at some subsequent meetings, the question whether the conditions necessary for such an inquiry could be realised was a burning one. This is no longer the case. The patient endeavours which were made about that time to obtain experimental proof of what was called *abiogenesis*, although they conduced materially to that better knowledge which we now possess of the conditions of life of bacteria, failed in the accomplishment of their purpose. The question still remains undetermined; it has, so to speak, been adjourned *sine die.* The only approach to it lies at present in the investigation of those rare instances in which, although the relations between a living organism and its environment ceases as a watch stops when it has not been wound, these relations can be re-established—the process of life re-awakening—by the application of the required stimulus.

I was also desirous to illustrate the relation between physiology and its two neighbours on either side, natural philosophy (including chemistry) and psychology. As regards the latter I need add nothing to what has already been said. As regards the former, it may be well to notice that although physiology can never become a mere branch of applied physics or chemistry, there are parts of physiology wherein the principles of these sciences may be applied directly. Thus, in the beginning of the century, Young applied his investigations as to the movements of liquids in a system of elastic tubes, directly to the phenomena of the circulation; and a century before, Borelli successfully examined the mechanisms of locomotion and the action of muscles, without reference to any, excepting mechanical principles. Similarly, the foundation of our present knowledge of the process of nutrition was laid in the researches of Bidder and Schmidt, in 1851, by determinations of the weight and composition of the body, the daily gain of weight by food or oxygen, the daily loss by the respiratory and other discharges, all of which could be accomplished by chemical means. But in by far the greater number of physiological investigations, both methods (the physical or chemical and the physiological) must be brought to bear on the same question—to co-operate for the elucidation of the same problem. In the researches, for example, which during several years have occupied Professor Bohr, of Copenhagen, relating to the exchange of gases in respiration, he has shown that factors purely physical—namely, the partial pressures of oxygen and carbon dioxide in the blood which flows through the pulmonary capillaries—are, so to speak, interfered with in their action by the "specific energy" of the pulmonary tissue, in such a way as to render this fundamental process, which, since Lavoisier, has justly been regarded as one of the most important in physiology, much more complicated than we for a long time supposed it to be. In like manner Heidenhain has proved that the process of lymphatic absorption, which before we regarded as dependent on purely mechanical causes—*i.e.*, differences of pressure—is in great measure due to the specific energy of cells, and that in various processes of secretion the principal part is not, as we were inclined not many years ago to believe, attributable to liquid diffusion, but to the same agency. I wish that there had been time to have told you something of the discoveries which have been made in this particular field by Mr. Langley, who has made the subject of "specific energy" of secreting cells his own. It is in investigations of this kind, of which any number of examples could be given, in which vital reactions mix themselves up with physical and chemical ones so intimately that it is difficult to draw the line between them, that the physiologist derives most aid from whatever chemical and physical training he may be fortunate enough to possess.

There is, therefore, no doubt as to the advantages which physiology derives from the exact sciences. It could scarcely be averred that they would benefit in anything like the same degree from closer association with the science of life. Nevertheless, there are some points in respect of which that science may have usefully contributed to the advancement of physics or of chemistry. The discovery of Graham as to the characters of colloid substances, and as to the diffusion of bodies in solution through membranes, would never have been made had not Graham "ploughed," so to speak, "with our heifer." The relations of certain colouring-matters to oxygen and carbon dioxide would have been unknown, had no experiments been made on the respiration of animals and the assimilative process in plants; and, similarly, the vast amount of knowledge which relates to the chemical action of ferments must be claimed as of physiological origin. So also there are methods, both physical and chemical, which were originally devised for physiological purposes. Thus the method by which meteorological phenomena are continuously recorded graphically originated from that used by Ludwig (1847) in his "Researches on the Circulation"; the mercurial pump, invented by Lothar Meyer, was perfected in the physiological laboratories of Bonn and Leipzig; the rendering the galvanometer needle aperiodic by damping was first realised by du Bois-Reymond—in all of which cases invention was prompted by the requirements of physiological research.

Let me conclude with one more instance of a different kind, which may serve to show how, perhaps, the wonderful ingenuity of contrivance which is displayed in certain organised structures—the eye, the ear, or the organ of voice—may be of no less interest to the physicist than to the physiologist. Johannes Müller, as is well known, explained the compound eye of insects on the theory that an erect picture is formed on the convex retina by the combination of pencils of light, received from different parts of the visual field through the eyelets (ommatidia) directed to them. Years afterwards it was shown that in each eyelet an image is formed which is reversed. Consequently, the mosaic theory of Müller was for a long period discredited on the ground that an erect picture could not be made up of "upside-down" images. Lately the subject has been re-investigated, with the result that the mosaic theory has regained its authority. Professor Exner,* has proved photographically that behind each part of the insect's eye an erect picture is formed of the objects towards which it is directed. There is, therefore, no longer any difficulty in understanding how the

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* Exner, "Die Physiologie der facettirten Augen von Krebsen u. Insecten," Leipzig, 1891.

whole field of vision is mapped out as consistently as it is imaged on our own retina, with the difference, of course, that the picture is erect. But behind this fact lies a physical question—that of the relation between the erect picture which is photographed and the optical structure of the crystal cones which produce it—a question which, although we cannot now enter upon it, is quite as interesting as the physiological one.

With this history of a theory which, after having been for thirty years disbelieved, has been reinstated by the fortunate combination of methods derived from the two sciences, I will conclude. It may serve to show how, though physiology can never become a part of natural philosophy, the questions we have to deal with are cognate. Without forgetting that every phenomenon has to be regarded with reference to its useful purpose in the organism, the aim of the physiologist is not to inquire into final causes, but to investigate processes. His question is ever How, rather than Why.

May I illustrate this by a simple, perhaps too trivial, story, which derives its interest from its having been told of the childhood of one of the greatest natural philosophers of the present century?* He was even then possessed by that insatiable curiosity which is the first quality of the investigator; and it is related of him that his habitual question was "What is the *go* of it?" and if the answer was unsatisfactory, "What is the particular go of it?" That North Country boy became Professor Clerk Maxwell. The questions he asked are those which in our various ways we are all trying to answer.

# ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

NOTTINGHAM, 1893.

By Professor EMERSON REYNOLDS, M.D., Sc.D., F.R.S., President of the Section.

At the Nottingham Meeting of the British Association in 1866, Dr. H. Bence Jones addressed the Section over which I have now the honour to preside on the place of Chemical Science in Medical Education. Without dwelling on this topic to-day, it is an agreeable duty to acknowledge the foresight of my predecessor as to the direction of medical progress. Twenty-seven years ago the methods of inquiry and instruction in medicine were essentially based on the formal lines of the last generation. Dr. Bence Jones saw that modern methods of research in chemistry—and in the experimental sciences generally—must profoundly influence medicine, and he urged the need of fuller training of medical students in those sciences.

The anticipated influence is now operative as a powerful factor in the general progress of medicine and medical education; but much remains to be desired in regard to the chemical portion of that education. In the later stages of it, undue importance is still attached to the knowledge of substances rather than of principles; of products instead of the broad characters of the chemical changes in which they are formed. Without this higher class of instruction it is unreasonable to expect an intelligent perception of complex physiological and pathological processes which are chemical in character, or much real appreciation of modern pharmacological research. I have little doubt, however, that the need for this fuller chemical education will soon be so strongly felt that the necessary reform will come from within a profession which has given ample proof in recent years of its zeal in the cause of scientific progress.

In our own branch of science the work of the year has been substantial in character, if almost unmarked by discoveries of popular interest. We may probably place in the latter category the measure of success which the skill of Moissan has enabled him to attain in the artificial production of the diamond form of carbon, apparently in minute crystals similar to those recognised by Koenig, Mallard, Daubrée, and by Friedel in the supposed meteorite of Cañon de Diablo in Arizona. Members of the Section will probably have the opportunity of examining some of these artificial diamonds through the courtesy of M. Moissan, who has also, at my request, been so good as to arrange for us a demonstration of the properties of the element fluorine, which he succeeded in isolating in 1887.

Not less interesting or valuable are the studies of Dr. Perkins, on electro-magnetic rotation; of Lord Rayleigh, on the relative densities of gases; of Dewar, on chemical relations at extremely low temperatures; of Clowes, on exact measurements of flame-cap indications afforded by Miner's testing lamps; of Horace Brown and Morris, on the chemistry and physiology of foliage leaves, by which they have been led to the startling conclusion that cane-sugar is the first sugar produced during the assimilation of carbon, and that starch is formed at its expense as a more stable reserve material for subsequent use of the plant; or of Cross, Bevan, and Beadle, on the interaction of alkali cellulose and carbon bisulphide, in the course of which they have proved that a cellulose residue can act like an alcohol radical in the formation of thiocarbonates, and thus have added another to the authors' valuable contributions to our knowledge of members of the complex group of celluloses.

But it is now an idle task for a President of this Section to attempt a slight sketch of the works of chemical philosophers even during the short space of twelve months; they are too numerous and generally too important to be lightly treated, hence we can but apply to them a paraphrase of the ancient formula—Are they not written in the books of the chronicles we term "Jahresberichte," "Annales," or "Transactions and Abstracts," according to our nationality?

I would, however, in this connection ask your consideration for a question relating to the utilisation of the vast stores of facts laid up—some might even say buried—in the records to which reference has just been made. The need exists, and almost daily becomes greater, for facile reference to this accumulated wealth, and of such a kind that an investigator, commencing a line of inquiry with whose previous history he is not familiar, can be certain to learn *all* the facts known on the subject up to a particular date, instead of having only the partial record to be found in even the best edited of the dictionaries now available. The best and most obvious method of attaining this end is the publication of a subject-matter index of an ideally complete character. I am glad to know that the Chemical Society of London will probably provide us in the years to come with a compilation which will doubtless aim at a high standard of value as a work of reference to memoirs, and in some degree to their contents, so far as the existing indexes of the volumes of the Society's Journal supply the information. Whether this subject-matter index is published or not, the time has certainly arrived for adopting the immediately useful course of publishing monographs, analogous to those now usual in Natural Science, which shall contain all the information gained up to a particular date in the branch of chemistry with which the author is specially familiar by reason of his own work in the subject. Such monographs should include much more than any mere compilation, and would form the best material from which a complete subject-matter index might ultimately be evolved.

My attention was forcibly drawn to the need of such special records by noting the comparatively numerous cases of re-discovery and imperfect identification of derivatives of thiourea. In my laboratory, where this

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* "Life of Clerk Maxwell" (Campbell and Garnett), p. 28.

substance was isolated, we naturally follow with interest all work connected with it, and therefore readily detect lapses of the kind just mentioned. But when it is remembered that the distinct derivatives of thiourea now known number considerably over six hundred substances, and that their descriptions are scattered through numerous British and foreign journals, considerable excuse can be found for workers overlooking former results. The difficulty which exists in this one small department of the science I hope shortly to remove, and trust that others may be induced to provide similar works of reference to the particular branches of chemistry with which they are personally most familiar.

When we consider the drift of investigation in recent years, it is easy to recognise a distinct reaction from extreme specialisation in the prominence now given to general physico-chemical problems, and to those broad questions concerning the relations of the elements which I would venture to group under the head of "Comparative Chemistry." Together these lines of inquiry afford promise of definite information about the real nature of the seventy or more entities we term "elements," and about the mechanism of that mysterious yet definite change in matter which we call "chemical action." Now and again one or other class of investigation enables us to get some glimpse beyond the known which stimulates the imaginative faculty.

For example, a curious side-light seems to be thrown on the nature of the elements by the chemico-physical discussion of the connection existing between the constitution of certain organic compounds and the colours they exhibit. Without attempting to intervene in the interesting controversy in which Armstrong and Hartley are engaged as to the nature of the connection, we may take it as an established fact that a relation exists between the power which a dissolved chemical compound possesses of producing the colour impression within our comparatively small visual range, and the particular mode of grouping of its constituent radicals in its molecule. Further, the reality of this connection will be most freely admitted in the class of aromatic compounds—that is, in derivatives of benzene—whose constituents are so closely linked together as to exhibit quasi-elemental persistence. If, then, the possession of what we call colour by a compound be connected with its constitution, may we not infer that "elements" which exhibit distinct colour, such as gold and copper, in thin layers and in their soluble compounds are at least complexes analogous to definitely decomposable substances? This inference, while legitimate as it stands, would obviously acquire strength if we could show that anything like isomerism exists among the elements; for identity of atomic weight of any two chemically distinct elements must, by all analogy with compounds, imply dissimilarity in constitution, and therefore definite structure, independently of any argument derived from colour. Now, nickel and cobalt are perfectly distinct elements, as we all know, but, so far as existing evidence goes, the observed differences in their atomic weights (nickel 58 6, cobalt 58·7) are so small as to be within the range of the experimental errors to which the determinations were liable. Here, then, we seem to have the required example of something like isomerism among elements, and consequently some evidence that these substances are complexes of different orders; but in the cases of cobalt and nickel we also know that in transparent solutions of their salts, if not in thin layers of the metals themselves, they exhibit strong and distinct colours; compare the beautiful rosy tint of cobalt sulphate with the brilliant green of the corresponding salt of nickel. Therefore, in exhibiting characteristically different colours, these substances afford us some further evidence of structural differences between the matter of which they consist, and support the conclusion to which their apparent identity in atomic weight would lead us. By means of such side-lights we may gradually acquire some idea of the nature of the elements, even if we are unable to get any clue to their origin other than such as may be found in Crookes's interesting speculations.

Again, while our knowledge of the genesis of the chemical elements is as small as astronomers possess of the origin of the heavenly bodies, much suggestive work has recently been accomplished in the attempt to apply the principle of gravitation, which simply explains the relative motions of the planets, to account for the interactions of the molecules of the elements. The first step in this direction was suggested by Mendeleeff in his Royal Institution lecture (May 31, 1889), wherein he proposed to apply Newton's third law of motion to chemical molecules, regarded as systems of atoms analogous to double stars. The Rev. Dr. Haughton has followed up this idea with his well-known mathematical skill, and, in a series of papers just published, has shown that the three Newtonian laws are applicable to explain the interactions of chemical molecules, "with this difference, that whereas the specific coefficient of gravity is the same for all bodies, independent of the particular kind of matter of which they are composed, the atoms have specific coefficients of attraction which vary with the nature of the atoms concerned." The laws of gravitation, with this proviso, were found to apply to all the definite cases examined, and it was shown that a chemical change of combination is equivalent to a planetary catastrophe. So far the fundamental hypothesis of "Newtonian Chemistry" has led to conclusions which are not at variance with the facts of the science, while it gives promise of help in obtaining a solution of the great problem of the nature of chemical action.

Passing from considerations of the kind to which I have just referred, permit me to occupy the rest of the time at my disposal with a short account of a line of study in what I have already termed "comparative chemistry," which is not only of inherent interest, but seems to give us the means of filling in some details of a hitherto rather neglected chapter in the early chemical history of this earth.

The most remarkable outcome of "comparative chemistry" is the periodic law of the elements, which asserts that the properties of the elements are connected in the form of a periodic function with the masses of their atoms. Concurrently with the recognition of this principle, other investigations have been in progress, aiming at more exact definitions of the characters of the relations of the elements, and ultimately of their respective offices in nature. Among inquiries of this kind the comparative study of the elements carbon and silicon appears to me to possess the highest interest. Carbon, whether combined with hydrogen, oxygen, or nitrogen, or with all three, is the great element of organic nature, while silicon, in union with oxygen and various metals, not only forms about one-third of the solid crust of the earth, but is unquestionably the most important element of inorganic nature. The chief functions of carbon are those which are performed at comparatively low temperatures; hence carbon is essentially the element of the present epoch. On the other hand, the activities of silicon are most marked at very high temperatures; hence it is the element whose chief work in nature was performed in the distant past, when the temperature of this earth was far beyond that at which the carbon compounds of organic life could exist. Yet between these dominant elements of widely different epochs remarkably close analogies are traceable, and the characteristic differences observed in their relations with other elements are just those which enable each to play its part effectively under the conditions which promote its greatest activity.

The chemical analogies of the two tetrad elements carbon and silicon are most easily recognised in compounds which either do not contain oxygen or which are oxygen compounds of a very simple order, and the following Table will recall a few of the most important of these, as well as some which have resulted from the fine researches of Friedel, Crafts, and Ladenburg:—

*Some Silicon Analogues of Carbon Compounds.*

| | | |
|---|---|---|
| $SiH_4$ | Hydrides | $CH_4$. |
| $SiCl_4$<br>$Si_2Cl_6$ | Chlorides | $CCl_4$.<br>$C_2Cl_6$. |
| $SiO_2$ | Oxides | $CO_2$. |
| $H_2SiO_3$ | Meta acids | $H_2CO_3$. |
| $HSiHO_2$ | Formic acids | $HCHO_2$. |
| $(SiHO)_2O$ | Formic anhydrides | $(CHO)_2O$ ? |
| $H_2Si_2O_4$ | Oxalic acids | $H_2C_2O_4$. |
| $HSi(CH_3)O_2$ | Acetic acids | $HC(CH_3)O_2$. |
| $HSi(C_6H_5)O_2$ | Benzoic acids | $HC(C_6H_5)O_2$. |
| $SiC_8H_{19}H$ | Nonyl hydrides | $C_9H_{19}H$. |
| $SiC_8H_{19}OH$ | Nonyl alcohols | $C_9H_{19}OH$. |

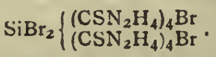
But these silicon analogues of carbon compounds are, generally, very different from the latter in reactive power, especially in presence of oxygen and water. For example, hydride of silicon, even when pure, is very easily decomposed, and, if slightly warmed, is spontaneously inflammable in air; whereas the analogous marsh gas does not take fire in air below a red heat. Again, the chlorides of silicon are rapidly attacked by water, affording silicon hydroxides and hydrochloric acid; but the analogous carbon chlorides are little affected by water even at comparative high temperatures. Similarly, silicon chloroform and water quickly produce silico-formic acid and anhydride along with hydrochloric acid, while ordinary chloroform can be kept in contact with water for a considerable time without material change.

Until recently no well-defined compounds of silicon were known including nitrogen; but we are now acquainted with a number of significant substances of this class.

Chemists have long been familiar with the fact that a violent reaction takes place when silicon chloride and ammonia are allowed to interact. Persoz, in 1830, assumed that the resulting white powder was an addition compound, and assigned to it the formula $SiCl_4,6NH_3$, while Besson, as lately as 1892, gave $SiCl_4,5NH_3$. These formulæ only express the proportions in which ammonia reacts with the chloride under different conditions, and give us no information as to the real nature of the product; hence they are almost useless. Other chemists have, however, carefully examined the product of this reaction, but owing to peculiar difficulties in the way have not obtained results of a very conclusive kind. It is known that the product when strongly heated in a current of ammonia gas affords ammonium chloride which volatilises and a residue, to which Schutzenberger and Colson have assigned the formula $Si_2N_3H$. This body they regard as a definite hydride of $Si_2N_3$, which latter they produced by acting on silicon at a white heat with pure nitrogen. Gattermann suggests that a nearer approach to the silicon analogue of cyanogen, $Si_2N_2$, should be obtained from the product of the action of ammonia on silicon chloroform; but it does not appear that this suggestion has yet borne fruit. It was scarcely probable that the above-mentioned rather indefinite compounds of silicon with nitrogen were the only ones of the class obtainable, since bodies including carbon combined with nitrogen are not only numerous, but are among the most important carbon compounds known. Further investigation was therefore necessary in the interests of comparative chemistry, and for special reasons which will appear later on; but it was evident that a new point of attack must be found.

A preliminary experimental survey proved the possibility of forming numerous compounds of silicon containing nitrogen, and enabled me to select those which seemed most likely to afford definite information. For much of this kind of work silicon chloride was rather too energetic, hence I had a considerable quantity of the more manageable silicon tetrabromide prepared by Serullas's method, viz., by passing the vapour of crude bromine (containing a little chlorine) over a strongly-heated mixture of silica and charcoal. In purifying this product I obtained incidentally the chloro-bromide of silicon, $SiClBr_3$, which was required in order to complete the series of possible chlorobromides of silicon.*

Silicon bromide was found to produce addition compounds very readily with many feebly-basic substances containing nitrogen. But one group of bromides of this class has yet been investigated in detail, namely, the products afforded by thioureas. The typical member of this group is the perfectly definite but uncrystalline substance—



$$SiBr_2\left\{\begin{matrix}(CSN_2H_4)_4Br\\(CSN_2H_4)_4Br\end{matrix}\right. .$$

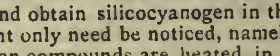
Substituted thioureas afford similar bodies, the most interesting of which is the allyl compound. This is a singularly viscid liquid, which requires several days at ordinary temperatures to regain its level, when a tube containing it is inverted. But these are essentially addition compounds, and are therefore comparatively unimportant.

In most cases, however, the silicon haloids enter into very definite reaction with nitrogen compounds, especially when the latter are distinctly basic, such as aniline or any of its homologues. One of the principal products of this class of change is the beautiful typical substance on the table, which is the first well-defined crystalline compound obtained in which silicon is exclusively combined with nitrogen. Its composition is $Si(NHC_6H_5)_4$.† Analogous compounds have been formed with the toluidines, naphthylamines, &c., and have been examined in considerable detail, but it suffices to mention them and proceed to point out the nature of the changes we can effect by the action of heat on the comparatively simple anilide.

When silicon anilide is heated carefully *in vacuo* it loses one molecule of aniline very easily and leaves triphenyl guanidine, probably the *a* modification; if the action of heat be continued, but at ordinary pressure and in a current of dry hydrogen, another molecule of aniline can be expelled, and, just before the last trace of the latter is removed, the previously liquid substance solidifies and affords a silicon analogue of the insoluble modification of carbodiphenyldiimide, which may then be heated moderately without undergoing further material change. A comparison of the formulæ will make the relations of the products clear:—

Silicotetraphenylamide—$Si(NHPh)_4$
Silicotriphenylguanidine—$Si : NPh.(NHPh)_2$
Silicodiphenyldiimide—$Si : (NPh)_2$.

Moreover, the diimide has been heated to full redness in a gas combustion furnace while dry hydrogen was still passed over it; even under these conditions little charring occurred, but some nitrogen and a phenyl radical were eliminated, and the purified residue was found to approximate in composition to $SiNPh$, which would represent the body as phenylsilicocyanide or a polymer of it. Even careful heating of the diimide in ammonia gas has not enabled me to remove all the phenyl from the compound, but rather to retain nitrogen, as the best residue obtained from such treatment consisted of $Si_2N_3Ph$, or the phenylic derivative of one of the substances produced by Schutzenberger and Colson from the ammonia reaction. It may be that both these substances are compounds of silicocyanogen with an imide group of the kind below indicated:—



$$\begin{matrix}SiN\\SiN\end{matrix}\!>\!NH \quad : \quad \begin{matrix}SiN\\SiN\end{matrix}\!>\!NPh.$$

Further investigation must decide whether this is a real relationship; if it be we should be able to remove the imidic group and obtain silicocyanogen in the free state. One other point only need be noticed, namely, that when the above silicon compounds are heated in oxygen they

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* Three years later Besson formed the same compound and described it as new.

† Harden has obtained an uncrystalline intermediate compound, $SiCl_2(NHC_6H_5)_2$.

are slowly converted into $SiO_2$; but the last traces of nitrogen are removed with great difficulty, unless water-vapour is present, when ammonia and silica are quickly formed.

Much remains to be done in this department of comparative chemistry, but we may fairly claim to have established the fact that silicon, like carbon, can be made to form perfectly well-defined compounds, in which it is exclusively united with the triad nitrogen of amidic and imidic groups.

Now, having proved the capacity of silicon for the formation of compounds of this order with a triad element, Nature very distinctively lets us understand that nitrogen is not the particular element which is best adapted to play the triad *rôle* towards silicon in its high-temperature changes, which are ultimately dominated by oxygen. We are not acquainted with any natural compounds which includes silicon and nitrogen; but large numbers of the most important minerals contain the pseudo-triad element aluminum combined with silicon, and few include any other triad. Phosphorus follows silicon in the periodic system of the elements as nitrogen does carbon, but silicates containing more than traces of phosphorus are rare; on the other hand, silicates are not uncommon containing boron, the lower homologue of aluminum; for example, axinite, datholite, and tourmaline.

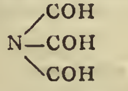
Moreover, it is well known that silicon dissolves freely in molten aluminum, though much of the former separates on cooling. Winkler has analysed the gangue of aluminum saturated with silicon, and found that its composition is approximately represented by the formula SiAl, or, perhaps, $Si_2Al_2$, if we are to regard this as analogous to $C_2N_2$ or cyanogen. Here aluminum at least resembles nitrogen in directly forming a compound with silicon at moderately high temperature. It would appear, then, that while silicon can combine with both the triads nitrogen and aluminum, the marked positive characters of the latter, and its extremely low volatility, suit it best for the production of permanent silicon compounds similar to those which nitrogen can afford.

With these facts in mind we may carry our thoughts back to that period in the earth's history when our planet was at a higher temperature than the dissociation point of oxygen compounds. Under such conditions the least volatile elements were probably liquids, while silicides and carbides of various metals were formed in the fluid globe. We can imagine that the attraction of aluminum for the large excess of silicon would assert itself, and that, as the temperature fell below the point at which oxidation became possible, these silicides and carbides underwent some degree of oxidation, the carbides suffering most owing to the volatility of the oxides of carbon, while the fixity of the products of oxidation of silicides rendered the latter process a more gradual one. The oxidation of silicides of metals which had little attraction for silicon would lead to the formation of simple metallic silicates and to the separation of the large quantities of free silica we meet with in the solid crust of the earth, whereas oxidation of silicides of aluminum would not break up the union of the two elements, but rather cause the ultimate formation of the alumino-silicates which are so abundant in most of our rocks.

Viewed in the light of the facts already cited and the inferences we have drawn from them as to the nitrogen-like relationship of aluminum to silicon, I am disposed to regard the natural alumino-silicates as products of final oxidation of sometime active silico-aluminum analogues of carbo-nitrogen compounds, rather than ordinary double salts. It is generally taken for granted that they are double salts, but recent work on the chromoxalates by E. A. Werner has shown that this view is not necessarily true of all such substances.

Without going into undue detail we can even form some conception of the general course of change from simple aluminum silicide to an aluminc-silicate, if we allow the analogies already traced to lead us further.

We recognise the existence of silico-formyl in Friedel and Ladenburg's silico-formic anhydride; hence silico-triformamide is a compound whose probable formation we can admit, and, on the basis of our aluminum-nitrogen analogy, an aluminum representative also. Thus—



Triformamide.

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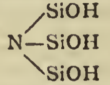

Silico-triformamide.

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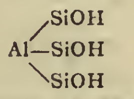

Silico-alumino-triformamide.

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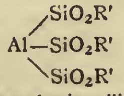
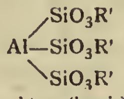


Salt of an alumino-silicic acid.

Now, oxidation of triformamide would lead to complete re-solution into nitrogen gas, carbon dioxide gas and water rendering it an extremely unstable body; under similar conditions silico-triformamide would probably afford nitrogen gas and silicic acid (or silicon dioxide and water); while the third compound, instead of breaking up, would (owing to the fixity of aluminum as compared with nitrogen) be likely at first to afford a salt of an alumino-silicic acid, in presence of much basic material.

The frequent recurrence of the ratios $Si_3Al, Si_3Al_2$, &c., in the formulæ of natural alumino-silicates, suggests that some at least of these minerals are derived from oxidation products of the above triformic type. Without stopping to trace all the possible stages in the oxidation of the primary compound $Al(SiO_2R)_3$, or variations in basicity of the products, I may cite the four following examples out of many others which might be given of resulting representative mineral groups:—



Beryl type (hemi-).

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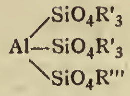

Garnet type.

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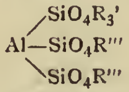

Muscovite type.

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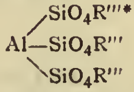

Xenolite type.

Five years ago Professor F. W. Clarke, of the United States Geological Survey, published a most interesting paper on the structure of the natural silicates. In this he adapts the view that the mineral xenolite, $Si_3Al_4O_{12}$, is the primary from which all other alumino-silicates may be supposed to arise by various substitutions. Nature, however, seems to teach us that such minerals as xenolite, fibrolite, and the related group of "clays" are rather to be regarded as end-products of a series of hydrolytic changes of less aluminous silicates than primary substances themselves; hence the sketch which I have ventured to give above of the probable genesis of alumino-silicates seems to provide a less arbitrary basis for Clarke's interesting work, without materially disturbing the general drift of his subsequent reasoning.

We may now consider for a moment in what direction evidence can be sought for the existence in nature of derivatives of the hypothetical intermediate products of oxidation between a primary silicide and its fully oxidised silicate.

In the absence of a working hypothesis of the kind which I have already suggested, it is not probable that direct evidence would yet be obtainable—this must be work for the future—but when we consider that the exist-

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* In these cases where R'''=Al it is, of course, assumed that the latter is acting only as a basic radical.

ence of compounds of the order in question would manifest themselves in ordinary mineral analyses by the analytical products exceeding the original weight of material, we seem to find some evidence on the point in recorded cases of the kind. A deficiency of a single atom of oxygen in compounds having the high molecular weights of those in question, would be indicated by very small excesses (from 2 to 3 per cent) whose real meaning might be easily overlooked. Now, such results are not at all unusual in analyses of mineral alumino-silicates. For instance, *Amphiboles* containing a mere trace of iron have afforded 102·75 parts from 100, and almost all analyses of *Microsommite* are high, giving as much as 103 parts. In less degree *Vesuvianite* and members of the *Andalusite* group may be noted. All these cases may be capable of some other explanations, but I cite them to show that such excesses are commonly met with in published analyses. On the other other hand, it is scarcely to be doubted that a good analyst, who obtained a really significant excess, would throw such a result aside as erroneous and never publish it. I therefore plead for much greater care in analyses of the kind in question, and closer scrutiny of results in the light of the suggestions I have ventured to offer. It is probable that silicates containing only partially oxidised aluminum are rare; nevertheless the search for them would introduce a new element of interest into mineralogical inquiries.

If the general considerations I have now endeavoured to lay before you are allowed their full weight, some of the alumino-silicates of our primary rocks reveal to us more than we hitherto supposed. Regarded from this newer standpoint, they are teleoxidised representatives of substances which foreshadowed in terms of silicon, aluminum, and oxygen the compounds of carbon, nitrogen, and hydrogen required at a later stage of the earth's history for living organisms. Thus, while the sedimentary strata contain remains which come down to us from the very dawn of life on this globe, the rocks from whose partial disintegration the preserving strata resulted contain mineral records which carry us still further back, even to Nature's earliest efforts in building up compounds similar to those suited for the purposes of organic development.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending July 31st, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, August 10th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples only one was recorded as "clear, but dull." All the others were clear, bright, and well filtered.

In our report for last month we drew attention to the long drought, which towards the end of June showed signs of breaking. The rainfall at the time of reporting was too slight to produce any difference in the quality of the waters. This month, however, the rain has been somewhat excessive, the total amount being 3·70 inches at Oxford, whereas the average fall for twenty-five years is 2·58 inches. The effect of this excess of rain is well seen in the following Table:—

| | Common salt per gallon. | Nitric acid per gallon. | Hardness. Degrees. | Oxygen required for oxidation per gallon. | Organic carbon per gallon. | Colour. | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Brown. | | Blue. |
| May | 2·196 | 0·611 | 14·66 | 0·029 | 0·062 | 11·3 | : | 20 |
| June | 2·155 | 0·601 | 14·74 | 0·033 | 0·065 | — | : | 20 |
| July | 2·114 | 0·674 | 13·96 | 0·036 | 0·070 | 15·9 | : | 20 |

The common salt and the hardness have diminished, consequent on the more flooded state of the river. The organic carbon and oxygen required to oxidise it have increased, but only in the third decimal place—a negligeable amount; and the brown colour is also slightly higher, all pointing to more organic matter in the July than in the June waters. At the same time the nitric acid has risen, showing that whatever the source of the organic matter might have been, the self-purifying power of the stream was well able to deal with the nitrogen present. The colour of the water points to a peaty origin for the organic matter, and this is borne out by the reduction in the amount of common salt, showing that the organic matter must have been chiefly of vegetable origin. Considering that July has experienced a sudden and excessive rainfall, following on one of the longest droughts on record, the excellent quality of the Metropolitan waters during the month points to a very high average standard of purity.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## ON ERBIA.*

By GERHARD KRÜSS

Mosander's investigations had shown in 1843 that the substance then known as yttria can be resolved into a yellow oxide and two colourless earths; he named the coloured earths erbia. The existence of such an earth was confirmed by Berlin in 1860, but it was again brought into question by Popp. By the researches of Delafontaine, and especially of Bahr and Bunsen, we finally reached the view that an erbia, a coloured yttrium earth, was really existent, and though by the further investigations of Marignac, Soret, Nilson, Cleve, Brauner, and others, further oxides, such as scandia, ytterbia, thulia, holmia (Soret's X), and terbia were separated from the erbia of the "sixties," the name erbia has up to the present day been retained for that earth which in its properties comes nearest to the former erbia. Among the group of the rare gadolinite earths precipitable by oxalic acid, erbia is that oxide which behaves more strongly basic than scandia and ytterbia, and also than Cleve's thulia, but is more feebly basic than Cleve's holmia, than terbia, and, above all, than yttria. Erbia ranges in colour from a tender rose to an amythest-red, and yields salts the solutions of which display in the absorption-spectrum the two

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* *Zeitschrift fur Anorganische Chemie.*

bands characterissic of erbium, Er $\alpha$ at $\lambda = 654{\cdot}7$ and Er $\beta$ at $\lambda = 523{\cdot}1$.

It must be mentioned that I have never been able to obtain an erbium preparation the solution of which on the examination of thick strata displayed merely the Er $\alpha$ and Er $\beta$ lines; there always occurred simultaneously some other lines, which are ascribed to holmium or to samarium. Many erbium preparations from the most different sources have been examined, including some in whose production more than 400 decompositions of nitrates have been executed.

The composition of erbium oxide was formerly taken as $ErO$, but it is now considered to be $Er_2O_3$. If we assume erbium as trivalent, we may calculate (according to the equivalent of erbia determined by P. T. Cleve and O. M. Höglund) for erbium the atomic weight of 170·4; subsequently it was determined by Humpidge and W. Burney = 171·3.

After characterising thulium $\overset{III}{Tm} = 171$, and holmium $\overset{III}{HO}$ about 161, Cleve finally found, in 1880, by the analysis of the sulphate, $\overset{III}{Er} = 166$. Subsequently no full investigation of erbia has been undertaken.

Some years ago I endeavoured to begin an examination of erbia ("Geschichte des Erbium and Didymium," *Liebig's Annalen*, cclxv., 1), as the spectroscopic examinations of L. F. Nilson and G. Krüss rendered it probable that erbia is not a unitary body. I endeavoured to furnish this proof, not in a physical but in a chemical manner. In the first place there resulted certain points of view with reference to the methods of examination and separation for the gadolinite earths, which have been communicated in *Liebig's Annalen* and in the *Zeitsch. fur Anorg. Chem.*, iii., 44, 60, 89, 92, 108.

In particular the behaviour of aniline and aniline hydrochlorate with the solutions of the earthy salts proved very valuable. The application of the "aniline method" in conjunction with the well-known method of decomposing the nitrates, decomposing the earthy nitrates by partial fractionation with heat, has rendered possible the results given below on the nature of erbia.

Such researches can at present be carried out only with a relatively large quantity of the costly material of the rare earths. I am therefore bound to declare my thanks to the Trustees of the "Elizabeth Thomson Science Fund" for the support which they have afforded me for carrying out my investigation on the nature of erbium.

At the same time I am greatly indebted to H. L. F. Nilson, of Stockholm, since he sent me the valuable material which he had acquired during the discovery of scandia and during the examination of ytterbia from the gadolinite earths. It was 404·5 grms. yttria earths ($\overset{III}{R} = 89$—92), 205·8 grms. of various holmia earths, 144·5 grms. erbium material, and 246·8 grms. ytterbia and thulia materials. If we consider what troublesome work is requisite to obtain such quantities of these earths in a relatively pure condition, we must highly appreciate the disinterested manner in which H. Nilson placed these specimens at my disposal.

The following experiments on erbia, holmia, and terbia were first made with rather smaller quantities of earths which I had prepared myself. Having thus felt my way, I took in hand the earths obtained from H. Nilson. The composition of the earths was ascertained, not merely spectroscopically, but by determining the equivalents of the earths. The methods were used described in *Zeitsch. f. Anorg. Chem.*, iii., 45—55. Before each determination of an equivalent, the earth to be analysed was carefully purified according to the instructions given in *Zeitsch. f. Anorg. Chem.*, iii., 48—49. In many cases it is sufficient to take for analysis only single fractions for the sake of a preliminary survey of the distribution of the several yttria-earths within a series of decompositions.

(To be continued).

## OBITUARY.

### C. W. HEATON, F.I.C., F.C.S.

The death is announced of Mr. C. W. Heaton, Professor of Chemistry in Charing Cross Hospital. Mr. Heaton commenced his studies first in the laboratory of Dugald Campbell and afterwards under Dr. Stenhouse in the laboratory of St. Bartholomew's Hospital, where he was Fellow Assistant with Professor Kekulé, Dr. Attfield, and the late Prof. Tuson, of the Royal Veterinary College, Camden Town; with the last-named two he enjoyed a life-long friendship. He subsequently acted as Assistant and Demonstrator in the Royal Veterinary College and at Charing Cross Hospital, and he finally succeeded to the post of Lecturer in the latter institution in 1862, a post which he held up to the time of his death. He undertook with conspicuous success the teaching of chemistry at Repton School, Tunbridge School, and Epsom College. Mr. Heaton was Examiner in Chemistry to the Royal College of Physicians and to the Royal College of Veterinary Surgeons, was Treasurer to the Society of Public Analysts, and filled the office of Public Analyst to the parish of St. Martin-in-the-Fields. He was also Lecturer to the London School of Medicine for Women. His literary works included contributions chiefly to the *Lancet*, to the *Saturday Review*, and to other Science Journals, as well as to various Art Journals. He re-edited and almost re-wrote "Stöckhardt's Chemistry," a text-book still in favour with students of medicine and others. He was connected with many important investigations of a technico-chemical character, and was interested to the last in the improved purification of coal-gas and of the recovery of sulphur therefrom. Mr. Heaton's personal character was such as to secure for him the high and universal esteem and respect of his brother chemists, whilst his pupils will ever remember him as a generous, kind, and painstaking teacher.

## MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Nottingham Meeting of the British Association:—

*President*—Prof. J. Emerson Reynolds, M.D., D.Sc., F.R.S., V.P.C.S.

*Vice-Presidents*—Prof. F. Clowes, D.Sc., F.C.S.; Prof. H. B. Dixon, M.A., F.R.S., F.C.S.; J. H. Gladstone, Ph.D., F.R.S.; Prof. H. McLeod, F.R.S., F.C.S.; W. H. Perkin, LL.D., Ph.D., F.R.S., V.P.C.S.; Prof. W. A. Tilden, D.Sc., F.R.S.

*Secretaries*—J. B. Coleman, F.C.S., A.R.C.Sc.; M. J. R. Dunstan, M.A., F.R.S.E.; D. H. Nagel, M.A., F.C.S.; W. W. J. Nicol, D.Sc., M.A., F.R.S.E., F.C.S. (Recorder).

*Committee*—A. H. Allen; C. H. Bothamley; H. T. Brown, F.R.S.; Prof. A. E. Dixon; T. Fairley; A. E. Fletcher; L. Fletcher; Prof. P. F. Frankland; G. Gladstone; A. Vernon Harcourt, F.R.S.; Prof. J. J. Hummel, H. Ingle; Dr. C. A. Kohn; Prof. V. B. Lewes; Dr. M. Meslans; S. U. Pickering, F.R.S.; Dr. S. Rideal; Dr. A. Richardson; Sir H. E. Roscoe, F.R.S.; Prof. A. Smithells; J. Spiller; Prof. J. E. Thorpe; T. Turner; W. Thomson; Dr. E. B. Truman; V. H. Veley; R. L. Whiteley.

The Papers brought before the Section were as follows:—

President's Address.

*Dr. J. H. Gladstone*—On Tools and Ornaments of Copper and other Metals from Egypt ahd Palestine.

Report of the Committee on International Standards for the Analysis of Iron and Steel.

*H. Harris and T. Turner*—On Native Iron Manufacture in Bengal.

*G. J. Fowler*—On Nitride of Iron.

Report of the Committee on the Silent Discharge of Electricity in Oxygen and other Gases.

Report of the Committee on the Action of Light on Dyed Colours.

*Dr. M. Meslans*—Demonstration of the Preparation and Properties of Fluorine by Moissan's Method.

Report of the Committee on the Formation of Haloids.

Report of the Committee on the Action of Light on the Hydracids of the Halogens in the presence of Oxygen.

*Dr. S. Rideal*—The Iodine-value of Sunlight in the High Alps.

*Dr. A. Richardson and J. Quick*—A Modified Form of Bunsen and Roscoe's Pendulum Actinometer.

*Dr. A. Richardson*—The Expansion of Chlorine and Bromine under the Influence of Light.

*Dr. C. A. Kohn*—The Cause of the Red Colouration of Phenol.

*Dr. Phookan*—The Rate of Evaporation of Bodies in Different Atmospheres.

*T. W. Hogg*—On the Occurrence of Cyano-nitride of Titanium in Ferro-Manganese.

Report of the Committee on the History of Chemistry.

Report of the Committee on the Wave Length Tables of the Spectra of the Elements.

Report of the Committee on the Bibliography of Spectroscopy.

Report of the Committee on the Bibliography of Solution.

Report of the Committee on Solution.

A Discussion on the Present Position of Bacteriology, more especially in its relation to Chemical Science, was opened by Prof. Percy F. Frankland.

*R. Warington, F.R.S.*—Remarks on the Chemistry of Bacteria.

*J. T. Wood*—Fermentation in connection with the Leather Industry.

*Dr. G. Tate*—On some Ferments derived from Diseased Pears.

*G. E. Brown and Dr. W. W. J. Nicol*—The Action of Permanganate of Potassium on Sodium Thiosulphate and Sulphite.

*Dr. S. Rideal*—The Application of Sodium Peroxide to Water Analysis.

Report of the Committee on Isomeric Naphthalene Derivatives.

*Dr. C. A. Kohn*—The Application of Electrolysis to Qualitative Analysis.

Report of the Committee on the Proximate Constituents of Coal.

*Dr. E. B. Truman*—Apparatus for the Extraction of Gases Dissolved in Water and other Liquids.

A Discussion on Explosions in Mines, with special reference to the Dust Theory, was introduced by Prof. H. B. Dixon.

*Prof. F. Clowes*—Hydrogen Flame Cap Measurements and the Adaptation of the Hydrogen Flame to the Miner's Safety Lamp.

*Prof. P. P. Bedson*—On the Gases Enclosed in Coal Dust.

*Prof. A. Smithells*—A Note on the Temperature and Luminosity of Gases.

*Bevan Lean*—Ethylbutane Tetracarboxylate and its Derivatives.

*W. J. Sell and T. H. Easterfield*—On the Salts of a New Sulphurea Base.

*W. J. Sell and T. H. Easterfield*—On Citrazinic Acid.

*Prof. F. Clowes*—On a Nottingham Sandstone containing Barium Sulphate as a Cemetery Material.

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Erratum.—P. 136, col. 2, line 9 from bottom, *or* "my," *read* "any."

THE CHEMICAL NEWS.

Vol. LXVII., No. 1766.

## AN INTERNATIONAL STANDARD FOR THE ANALYSIS OF IRON AND STEEL.*

In the previous report of this Committee it was mentioned that so far as the original four steel standards were concerned the work of the British analysts was completed. It was also stated that the American Committee had nearly finished its labours on these standards, and hoped to publish the results in a few months. Owing to the long distances over which the members of the American Committee are scattered, and the fact that some of the members of the Committee have still been labouring at the question of methods of carbon determination, it was not found possible to hold a meeting as originally intended, but the results of the analyses were to be communicated to, and the questions raised discussed at, the World's Congress of Chemists at Chicago. Professor Langley has, however, forwarded an advance report of the analyses, which is appended, together with the values obtained by the British analysts, which are added for comparison; the American results are subject to slight revision at Chicago, and should any alterations be made these will be inserted before this report is finally published.

I.—*Mean Results of the Analyses by the American Committee.*

| Standard. | No. 1. | No. 2. | No. 3. | No. 4. |
|---|---|---|---|---|
| Carbon .. .. | 1·44 | 0·80 | 0·454 | 0·18 |
| Silicon .. .. | 0·270 | 0·202 | 0·152 | 0·015 |
| Sulphur .. .. | 0·004 | 0·004 | 0·004 | 0·038 |
| Phosphorus .. | 0·016 | 0·010 | 0·015 | 0·088 |
| Manganese .. | 0·254 | 0·124 | 0·140 | 0·098 |

II.—*Mean Results of the Analyses by the British Committee.*

| Standard. | No. 1. | No. 2. | No. 3. | No. 4. |
|---|---|---|---|---|
| Carbon .. .. .. .. .. | 1·414 | 0·816 | 0·476 | 0·151 |
| Silicon .. .. .. .. .. | 0·263 | 0·191 | 0·141 | 0·008 |
| Sulphur, not more than.. | 0·006 | 0·007 | 0·008 | 0·039 |
| Phosphorus .. .. .. | 0·018 | 0·014 | 0·021 | 0·078 |
| Manganese .. .. .. | 0·259 | 0·141 | 0·145 | 0·130 |

A report has also been forwarded by Professor Akerman on behalf of the Swedish Committee, but as the results included in this report have not yet been revised, they are intended for the guidance of the other Committees, and not for publication. It may, however, be stated that the agreement between the Swedish and British reports is quite as good as that between the two above given.

Standard 5, the preparation of which was mentioned in the previous report of this Committee, has been hermetically sealed in glass tubes, like Standards 1, 2, 3, and 4. It was thought well not to proceed with the analysis of this standard until an opportunity had been afforded of comparing the results obtained by the various Committees on the analyses of the standards already under examination. Otherwise, after the work of the British analysts was completed, questions as to methods of analysis or other points of detail might have arisen, without a convenient opportunity being afforded for their investigation.

Now that reports from three out of the five International Committees are at hand for comparison, they will be considered by this Committee, and the analysis of the remaining standard completed.

## THE INFLUENCE OF THE SILENT DISCHARGE ON OXYGEN AND OTHER GASES.*†

This Committee was first appointed in 1885; grants of money were made in that and in the succeeding year. The expenditure of these grants has already been duly reported. It therefore now only remains to give an account of the work that has been done. This has already been fully described in the *Journal of the Chemical Society* and elsewhere, and consequently it will be sufficient now to give an outline of the results obtained, with references to the fuller descriptions.

### I.—*The Preparation and Storage of Oxygen.*‡

In this note a method of preparing oxygen from a mixture of the chlorates of sodium and potassium was described. The process recommended has been found to be very convenient, and has since been adopted by other investigators. Its advantage lies in the ready fusibility of the mixture, and the consequent reduced risk of breaking glass apparatus in which the chlorate must be submitted to repeated fusion and solidification in the course of generating oxygen from it.

### II.—*Ozone from Pure Oxygen. Its Action on Mercury, with a Note on the Silent Discharge of Electricity.*§

*By* W. A. Shenstone *and* J. Tudor Cundall.

The experiments described in this paper showed that a good yield of ozone (7·5 per cent) is readily obtained from carefully dried oxygen.

It has lately been suggested by Professor Armstrong that, in spite of the care taken, it is possible impurity may have been introduced into the gas by the action of the discharge, which might conceivably detach adherent moisture from the glass surfaces of the apparatus. Moreover, when these experiments were made the only liquid that was available for use in the manometers was oil of vitriol, and though this was screened from the dried oxygen by phosphoric anhydride, its use introduced a fresh element of uncertainty.

On the other hand, the proportion of ozone obtained was, considering the form of apparatus employed, sufficiently high to suggest that the conditions of the experiment were very favourable to the production of a high yield of ozone, and the mixture of ozone and oxygen obtained by the discharge was apparently without *chemical* action on mercury, which is inconsistent with the idea that moisture was present in it, whilst it is stated by Brodie in his "Classical Research" that in order to obtain a high yield of ozone *dry* oxygen must be employed.

The later experiments described in Section III. will make it possible now to investigate this point more severely than in 1885, and therefore this important question will very shortly be re-examined.

### III.—*Studies on the Formation of Ozone from Oxygen.*||

*By* W. A. Shenstone *and* Martin Priest.

The introduction of improved methods of working with ozone have enabled the authors of this paper to study the

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[*] Fifth Report of the Committee, consisting of Professor W. C. Roberts-Austen (Chairman), Sir F. Abel, Mr. E. Riley, Mr. J. Spiller, Professor J. W. Langley, Mr. G. J. Snelus, Professor Tilden, and Mr. Thomas Turner (Secretary). (Drawn up by the Secretary). Read before the British Association (Section B), Nottingham Meeting, 1893.

[*] Report of a Committee, consisting of Professor H. McLeod (Chairman), Mr. W. A. Shenstone (Secretary), Professor W. Ramsay, and Mr. J. Tudor Cundall. (Drawn up by the Secretary).

[†] Read before the British Association (Section B), Nottingham Meeting, 1893.

[‡] "British Assoc. Rep., 1886.

[§] *Journ. Chem. Soc.*, 1887.

[||] *Journ. Chem. Soc.*, 1893.

influence of various conditions on the converting of oxygen into ozone with increased exactness and facility.

The results obtained show that:—

1. Under constant conditions it is possible to obtain concordant results in converting oxygen into ozone by the silent discharge.

2. That the maximum yield of ozone is nearly independent of the difference of the potential employed to produce the discharge (the range of potential difference employed was from 33 to 69 C.G.S. units), provided that the path of the discharge be not too short.

3. That if the path of the discharge be very short, then the maximum yield of ozone has an inverse relation to the difference of potential employed.*

4. The rapidity with which the discharge converts oxygen into ozone is greater when great potential differences are employed than for smaller differences.

5. That the maximum yield of ozone is less when the number of discharges is *very* great in unit time than when it is smaller.† But the yield is not affected by moderate variations of rapidity of the discharge.

6. The greatest yield of ozone was obtained by using an ozone generator made of the thinnest possible glass, and with closely-fitting tubes. In one case 17·15 per cent of ozone was obtained at 0°.

7. Under equal conditions less ozone was produced by the discharge obtained by means of a Wimshurst's machine than when a large induction coil was employed.

It has been suggested that this last phenomenon may be due to a difference in the quantity of electricity acting in the two cases, but the authors point out that under the conditions of their experiments‡ the "quantity" of the discharge inside the ozone generator depends on the difference of potential of the inducing charge, and that as the ozonising effect of the discharge is, under suitable conditions (see 2 and 3 above), independent of the potential difference of the inducing charge, it would seem that this suggestion does not afford a clue to the cause of the phenomenon. Moreover, it was found in the experiments made with the plate machine that when the quantity of the inducing charge was raised or reduced, by means of condensers, the yield of ozone remained unaffected.

Although a good deal of progress has now been made, much of the work undertaken remains to be done. As, however, no further grants are likely to be asked for, and as it is probable that in the future the work will be mainly in the hands of one member of the Committee, the Committee now recommends that it be not re-appointed.

## ON NITRIDE OF IRON.§

By G. J. FOWLER, M.Sc.

This research was undertaken with the object of repeating and extending the work of Stahlschmidt (*Pogg. Ann.*, v., cxxv., 1865, p. 37) on the same subject, his results differing in many points from those of his predecessors.

The best way of preparing nitride of iron was found to be the following:—Iron is reduced from the hydrate by hydrogen, in a tube of such dimensions that it can be weighed, together with its contents, and thus the end of the reaction determined without exposing the iron to the air. When complete reduction has been effected, the iron is heated in a fairly rapid current of ammonia gas, until no further increase in weight is observed. The temperature should be kept a little above the melting-point of lead.

The product obtained when the reaction was complete was analysed. The nitrogen was determined by dissolving the substance in hydrochloric acid, evaporating with platinum chloride, and weighing the ammonium-platinum chloride obtained.

The hydrogen given off on solution of the substance in sulphuric acid was measured.

The iron was determined by ignition and weighing as oxide, and by solution in sulphuric acid and titration with permanganate.

As will be seen from the results obtained, the nitride prepared as above has a composition corresponding to the formula $Fe_2N$. On solution in hydrochloric acid the following reaction takes place:—

$$Fe_2N + 5HCl = 2FeCl_2 + NH_4Cl + H.$$

| | Found. | Calculated for $Fe_2N$. |
|---|---|---|
| N .. .. | 11·07 .. .. .. .. .. | 11·11 |
| Fe .. .. | 88·46 (mean of two titrations)<br>88·43 (by ignition) | 88·89 |
| H .. .. | 23·1 c.c. from 0·275 subst. .. | 24·4 c.c. |

In another sample 10·94 N was found. In a third case, in which the iron, after solution of the nitride in acid, was precipitated by ammonia and weighed as oxide, 89·44 per cent of iron was obtained and 10·5 per cent of nitrogen, showing again that the substance dissolves in acid according to the above equation, all the nitrogen being converted into ammonia.

No percentage of nitrogen above 11·1 could be obtained, while any percentage below that could be got according to the time during which the iron had been exposed to the current of ammonia.

These results are fully in agreement with those obtained by Stahlschmidt, and confirm his conclusion that only one nitride of iron exists, and that it has the above composition.

Nitride of iron is formed when iron amalgam is heated in ammonia, and also when ferrous chloride or bromide is heated in this gas. These methods, however, do not so readily give a product containing the full percentage of nitrogen, and free from the presence of a third element.

Nitride of iron is a grey powder, rather less blue in tone than iron reduced from the hydrate. On rubbing it is more gritty than iron prepared as above. It is feebly magnetic.

Heated in hydrogen, ammonia is produced at about the same temperature as that at which the nitride is formed.

It readily burns in chlorine, ferric chloride and nitrogen being formed.

Heated in carbon monoxide, no evidence of the formation of cyanogen compounds could be obtained.

Steam at 100° slowly oxidises the nitride, with evolution of ammonia.

Hydrogen sulphide begins to react with it at 200°, forming ammonium sulphide and sulphide of iron.

Heated in nitrogen to the boiling-point of sulphur, no change occurs. The temperature at which nitrogen is evolved by the action of heat alone must therefore be above this point.

An ethereal solution of iodine is without action upon the nitride.

From a slightly acidified solution of copper sulphate, nitride of iron deposits copper.

Heated with ethyl iodide to 200° in a sealed tube, olefines are formed, and iodides of iron and ammonium, the reaction evidently being—

$$5C_2H_5I + Fe_2N = 2FeI_2 + NH_4I + 5C_2H_4 + H.$$

Heated similarly to 200° with phenol, no reaction occurred.

Treated with a mixture of hydrogen peroxide and sulphuric acid, analyses showed that very little, if any, of the nitrogen is oxidised, the whole dissolving as usual to form ammonium sulphate.

In conjunction with Mr. P. J. Hartog, the author has

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* This is attributed to the difficulty of maintaining a sufficiently regular temperature of the gas under these circumstances.

† This is also probably due to imperfect refrigerating.

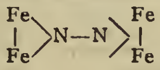
‡ Ozonisers of Brodie's type were employed.

§ A Paper read before the British Association (Section B), Nottingham Meeting, 1893.

determined the heat of formation of the nitride by dissolving it in sulphuric acid contained in a platinum calorimeter, and observing the rise of temperature. Three well-agreeing experiments showed that the substance is formed with evolution of about three calories.

In general the nitride of ammonia behaves as an ammonia derivative, the nitrogen being either evolved in the free state, or converted into ammonium compounds, according to circumstances.

Its possible constitution may be—



## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending August 31st, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, September 7th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples six were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

The long-continued dry-weather, which had lasted from March to the middle of June, showed signs of breaking during the latter month, and when writing our last month's report we were able to say that the rainfall for July had been 3·70 inches at Oxford, whereas the mean fall for twenty-five years was 2·58 inches, showing an excess of 1·12 inches. The effect of this was shown in a table, by which it was seen that the sudden and excessive rainfall, following one of the longest droughts ever recorded, was extremely slight in respect to the variation in quality of the metropolitan water, and imperceptible in respect to any injurious tendency.

The excessive rainfall was not kept up during August. The mean fall for this month, over an average of twenty-five years, is 2·24 inches at Oxford, while the actual fall has only been 1·01 inch, showing a deficiency of 1·23 inch. During the whole of the month there were only two really wet days, namely, the 4th, on which 0·35 inch, and the 22nd, on which 0·26 inch of rain fell; the rest of the month's rain, amounting to four-tenths of an inch, being distributed over eight days. The excess of rain in July being 1·12 inch, and the deficiency in August being 1·23 inch, it is seen that for the two months the rain has been 0·11 inch below the twenty-five years' mean, whilst, including June, the three months' deficiency amounts to 1·55 inch.

The dry August following the wet July has had the effect of minimising the divergences from the mean, which were shown in tabular form in our last month's report. The following Table shows the most noteworthy points on which comment may be desirable:—

| | Common salt per gallon. | Nitric acid per gallon. | Oxygen required per gallon. | Organic carbon per gallon. | Organic carbon per gallon. | Colour. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Brown. | Blue. |
| | Means. | Means. | Means. | Means. | Maxima. | Means. | |
| June | 2·155 | 0·601 | 0·033 | 0·065 | 0·083 | — | — |
| July | 2·114 | 0·674 | 0·036 | 0·070 | 0·098 | 15·9 : | 20 |
| Aug. | 2·161 | 0·705 | 0·034 | 0·067 | 0·084 | 15·3 : | 20 |

The common salt has slightly risen, as would be expected, from diminished dilution. The organic matter is a little less, as shown alike by the combustion test, the less amount of oxygen required for its oxidation, and the slightly diminished colour.

The colour, being of a vegetable, peaty origin, is higher than it is in colder weather, but the brown colour is a little less than it was in July. The nitric acid has risen, but only in the second decimal place, showing that, whatever the organic matter may have been at its entrance into the river, it has undergone efficient destruction before it leaves the Companies' reservoirs.

From the 21st to the 28th of August the colour of the water supplied by the Chelsea Company was somewhat below its usual high level. This was caused by a serious burst which occurred in one of their large 30-inch pumping mains. For a few days during repair the velocity of the water in the mains had to be retarded, occasioning a temporary deposit of harmless iron oxide. When the ordinary rate of flow was resumed some of this deposit was carried through the mains and caused a temporary discolouration, but in no case was the colour high enough to occasion a deficiency in brightness.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## ON THE ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 132).

### Thymol ($C_{10}H_{14}O$).

*Products Obtained with Excessive Dilution at 15° C.*

An alkaline solution of thymol was prepared containing 1 grm. thymol and about 1·5 grms. caustic soda in about 5 litres of water, and to this was added a large excess of decinormal solution of iodine, when there was soon obtained a bulky precipitate of yellowish brown colour, which was collected, washed, and dried. This was dissolved in ether, filtered, recovered, and dried. It was then treated with successive quantities of boiling alcohol as long as anything was dissolved out, the alcoholic solutions being filtered off. The portion soluble in alcohol was then recovered and dried. It was of an orange-yellow colour, of sticky character, and melted about 56° C.

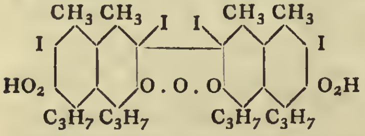
Total iodine of the alcohol-soluble portion:—
Quantity taken = 0·0924 grm.
Silver iodide found = 0·0818 ,, = 47·83 p.c. iodine.

The remainder of the alcohol-soluble portion was heated with water and copper in sealed tube for an hour at 60° C. The contents were then rinsed out and dried on water-bath, and the product dissolved out with ether, filtered, and recovered. Product of a whitish colour, melting with decomposition about 72° C.

Total iodine of this product:—
Quantity taken =0·1121 grm.
Silver iodide found=0·0948 „ =45·69 p.c. iodine.

Combustion of same:—
Quantity taken =0·0930 grm.
Water found =0·0342 „ = 4·08 p.c. hydrogen.
Carbon dioxide found =0·1352 „ =39·64 p.c. carbon.
By difference .. .. =10·59 „ oxygen.
Slight ash.

Those results may be well represented by the formula $C_{36}H_{42}I_4O_7$, or constitutionally thus:—



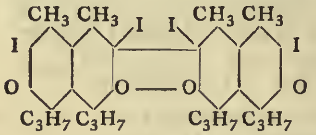
Theoretical:—
C =39·49
H = 3·84
I =46·43
O =10·24

The remainder of the precipitate insoluble in boiling alcohol was treated with ether, in which it readily dissolved. The ether was allowed to evaporate and the residue dried. It was of a slightly yellowish white colour, of pulverulent character, quite amorphous, and melted with decomposition.

Total iodine of the alcohol insoluble portion:—
Quantity taken =0·1070 grm.
Silver iodide found =0·0966 „ =48·78 p.c. iodine.

Combustion of same:—
Quantity taken =0·1142 grm.
Water found =0·0396 „ = 3·85 p.c. hydrogen.
Carbon dioxide found =0·1710 „ =40·83 p.c. carbon.
By difference .. .. = 6·54 „ oxygen.
Slight ash.

Those results may be well represented by the formula $C_{36}H_{40}I_4O_4$, or constitutionally thus:—



Theoretical:—
C =41·09
H = 3·83
I =48·66
O = 6·13

(Special hydrogen determination).

*Products Obtained with Moderate Dilution and at a Temperature of 60° C.*

There was taken 1 grm. thymol and 1·5 grm. caustic soda in 1 litre of water, the whole heated to 60°, and the iodine added as before. The precipitate obtained was of a brick-red colour, non-adhesive, and pulverulent. It was dissolved in ether, the solution filtered, the ether evaporated off, and the residue dried. It was then heated in an air chamber at about 100° C. until it had lost its red colour. This loss of colour was due to the driving off of what I may term the "encluded" iodine, which I have already dealt with under the character of "loosely-combined iodine" when treating of the simple phenol series. This "encluded" iodine is much more easily got rid of in the present series.

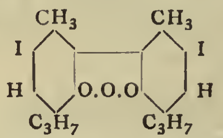
Total iodine of the whole precipitate:—
Quantity taken =0·1270 grm.
Silver iodide found =0·1086 „ =46·20 p.c. iodine.

The precipitate was treated with boiling alcohol and the soluble portion recovered. When dried it was of a light yellow colour, of sticky character, and amorphous, melting with decomposition about 88° C.

Total iodine of the alcohol-soluble portion:—
Quantity taken =0·2405 grm.
Silver iodide found =0·1997 „ =44·88 p.c. iodine.

Combustion of same:—
Quantity taken =0·0924 grm.
Water found =0·0347 „ = 4·17 p.c. hydrogen.
Carbon dioxide found =0·1423 „ =42·00 p.c. carbon.
By difference .. .. = 8·42 „ oxygen.
Slight ash.

Those results may be fairly well represented by the formula $C_{20}H_{22}I_2O_3$, or constitutionally thus:—



Theoretical:—
C =42·55
H = 3·90
I =45·03
O = 8·51

The residue from the alcohol-soluble portion of the precipitate was dissolved in ether and recovered. It was of whitish colour, pulverulent, and melted with decomposition about 172° C.

Total iodine of the alcohol-insoluble portion:—
Quantity taken =0·2203 grm.
Silver iodide found =0·1839 „ =45·10 p.c. iodine.

Combustion of same:—
Quantity taken =0·1246 grm.
Water found =0·0470 „ = 4·19 p.c. hydrogen.
Carbon dioxide found =0·1963 „ =42·96 p.c. carbon.
By difference .. .. = 7·75 „ oxygen.

It is pretty evident that the two portions of the precipitate were practically of the same composition. The great difference observed in the melting-points was undoubtedly due to the presence of practically free iodine in the alcohol-soluble portion, to which it owed its yellow colour, although it was no doubt also influenced by the quantity of hydrogen contained in the molecule, a difference of two atoms of hydrogen belonging to the benzene nuclei causing a large difference in the melting-point.

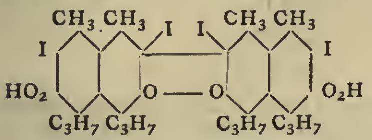
The red colour of the thymol product is not a peculiarity of the physical conditions predominating in such case as that just treated, as is evidenced by the following:— A new batch was set up under conditions similar to those used in the preparation of the yellow product (ordinary temperature and excessive dilution), with the only difference that a fresh sample of caustic soda was used containing a larger percentage of real hydrate. The precipitate obtained in this case was of a brick-red colour, of pulverulent character, similar in appearance to that obtained at 60° C., with a dilution of one litre, but was rather more readily fusible.

This precipitate was treated with boiling alcohol, the soluble portion filtered off, and the insoluble portion only examined.

Total iodine of the alcohol-insoluble portion:—
Quantity taken =0·1240 grm.
Silver iodide found=0·1077 „ =46·92 p.c. iodine.

Combustion of same:—
Quantity taken =0·1294 grm.
Water found =0·0484 „ = 4·15 p.c. hydrogen.
Carbon dioxide found =0·1910 „ =40·25 p.c. carbon.
By difference .. .. = 8·68 „ oxygen.

Those results may be well represented by the formula $C_{36}H_{42}I_4O_6$, or constitutionally thus:—



Theoretical:—
C = 40·07
H = 3·89
I = 47·12
O = 8·90

(To be continued).

## THE ACTION OF LIGHT UPON DYED COLOURS.*

THE object of the Committee appointed to study this matter has been to determine by experiment the relative fastness to light of the colours dyed on textile fabrics with the various natural and artificial colouring-matters.

For this purpose patterns of silk, wool, and cotton have been dyed with equal percentages (2 per cent) of the various commercial artificial colouring matters. With the natural colouring-matters the patterns were dyed to approximately the same depth of colour.

The patterns were exposed to light at Adel, a country district about five miles to the north of Leeds, in order to avoid the influence of town smoke, sulphurous acid, &c., the prevailing winds being westerly. The patterns were pinned on deal boards covered with white calico, fixed in a vertical position in glazed wooden cases, so arranged as to permit free circulation of the air and moisture after filtration through cotton-wool to exclude dust, &c.

The exposing cases were set up in the grounds of Jas. A. Hirst, Esq., to whom the best thanks of the Committee are due for his kind permission to do so.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. The shortest period of exposure, or "fading period," was about three weeks (May 24 to June 14, 1892), and a record of the fading power of this period was kept by exposing along with the patterns a special series of "standards" dyed with the selected colouring-matters. These standards were removed from the action of the light along with the first set of dyed patterns at the end of the first "fading period" (May 24 to June 14, 1892). The faded standards were then at once replaced by a fresh unexposed series, and these were allowed to fade to the same extent as the first, when, a second period of exposure equal in fading power to the first having thus been marked off, a second set of the dyed patterns were removed from the action of light along with the second series of faded standards. The latter were again renewed as before to mark off the next "fading period." The fourth and fifth sets of dyed patterns were submitted to an exposure equivalent to two or three "fading periods," in order that the fifth set might have an exposure of one year.

The above method was adopted in order to be able to expose dyed patterns to an equal amount of fading in different years, irrespective of the time of the year or the conditions of light, moisture, temperature, &c. It was rendered necessary indeed in consequence of the practical impossibility of exposing simultaneously a complete set of dyed colours.

During the year 1892—93 the red dyes on wool and silk have been exposed. For want of sufficient exposing space, however, the Congo colours and some others, as well as the reds dyed on cotton, had to be omitted. During 1893—94 the orange and yellow dyes are being exposed, and the remaining colours will be exposed in subsequent years until all have been examined. There is no doubt that the behaviour of dyed colours towards light and other agencies depends upon several factors, *e.g.*, the chemical constitution of the colouring-matter itself, the kind of fibre to which it is applied, the method of application, &c. With so many variables a full and complete examination of the question of the fastness of dyes proves to be one of extreme complexity and difficulty. Even to determine effectually the nature of the relationship existing between the molecular constitution of colouring-matters and their behaviour towards light seems to necessitate the employment of chemically pure dye-stuffs, and that the dyeing should be so arranged as to have an equal number of molecules of colouring-matter on a given weight of textile material. Having regard, therefore, to the difficulties connected with the purification of such a large number of colouring-matters as are now in use, their varying colouring-power, the different degree to which they exhaust the dye-bath, &c., it seemed better, for the present at least, to confine our attention to a comparison of the relative fastness to light of the various distinct commercial colours, the results of which might form a basis for a further examination in the direction alluded to.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during the year 1892—93, the colours being divided, according to their behaviour towards light, into the following five classes:—Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern-books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

### CLASS I.—*Very Fugitive Colours.* (*Wool*).

The colours of this class have faded so rapidly that at the end of the first "fading period" (May 24 to June 14, 1892) only a very faint colour remains, and at the end of the fifth period (one year) all traces of the original colour have disappeared, the woollen cloth being quite white or of a yellowish tint.

*Triphenylmethan Colours. Phthaleïns.*

Wool Book II.

*Eosins.*—

1. Eosin A. Alkali salt of tetra-brom-fluorescein. S. and J. 319.
2. Erythrosin G. Alkali salt of di-iodo-fluorescein. S. and J. 324.
3. Methyl-eosin. Potassium salt of tetra-brom-fluorescein-methyl-ether. S. and J. 320.
4. Erythrosin JN pure.
5. Eosin S. Potassium salt of tetra-brom-fluorescein-ethyl-ether. S. and J. 321.
6. Eosin F.
7. Phloxin P. Potassium salt of tetra-brom-di-chlor-fluorescein. S. and J. 325.
8. Eosin BN. Potassium salt of di-brom-di-nitro-fluorescein. S. and J. 322.
9. Erythrosin B. Sodium salt of tetra-brom-tetra-chlor-fluorescein. S. and J. 328.
10. Cyanosin (spirit soluble). Potassium salt of tetra-brom-di-chlor-fluorescein-methyl-ether. S. and J. 326.
11. Cyanosin B. Sodium salt of tetra-brom-tetra-chlor-fluorescein-ethyl-ether. S. and J. 329.
12. Phloxin tetra (pure).
13. Rose Bengale NTO.
14. Phloxin.
15. Rose Bengale NT pure.
16. Bengaline PH.

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* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Nottingham Meeting, 1893.

17. Bengal red B. Potassium salt of tetra-iodo-tetra-chlor-fluorescein. S. and J. 330.
18. Cyclamine. Eosin from the thio-dichlor-fluorescein. S. and J. 334.

### *Azine Colours. Safranines, &c.*

*Basic Reds.*—

6. Safranine B extra. From 1 mol. $p$-phenylene-diamine and 2 mols. aniline. S. and J. 356.
7. Safranine T extra. From 1 mol. $p$-toluylene-diamine, 1 mol. aniline, 1 mol. $o$-toluidine. S. and J. 358.
8. Diamido-phenazin-nitrate.
9. Neutral red. From dimethyl-diamido-toluphenazine hydrochloride. S. and J. 253.
11. Fuchsia. From 1. mol. dimethyl-$p$-phenylene-diamine and 2 mols. aniline. S. and J. 357.

### *Induline Colours. Rosindulines.*

Wool Book I.

*Acid Reds.*—

9. Rosinduline 2 G.
30. Rosinduline G.

### *Azo Colours.*

*Acid Reds.*—

43. Roxamine. From azo-deriv. of naphthionic acid and dioxynaphthalene (2·7).

NOTES.—Among the eosins, eosin BN is distinctly faster than the rest. Cyanosin B fades as rapidly as the rest during the first "fading period," but the pale tint then left is remarkable for its fastness, since it remains almost unchanged even after a year's exposure.

The eosins, rosindulines, and roxamine do not alter in tint when fading, but the safranines leave, at the end of the first "fading period," a dull brownish pink tint.

### CLASS II.—*Fugitive Colours.* (*Wool*).

The colours of this class show very marked fading at the end of the second "fading period" (June 14 to July 21, 1892), and after a year's exposure they have entirely faded, or only a tint remains.

### *Triphenylmethan Colours. Rosanilines.*

Wool Book II.

*Basic Reds.*—

12. Fuchsin MN.
13. Para-rosaniline. Para-rosaniline (base).
14. Rosaniline. Rosaniline (base).
15. Acetic acid Rubin. Rosaniline acetate.
16. Magenta. Rosaniline hydrochloride.
17. New magenta. Trimethyl-$p$-rosaniline hydrochloride.

Wool Book I.

*Acid Reds.*—

99. Acid Magenta. Alkaline salt of rosaniline-tri-sulphonic acid. S. and J. 279.

### *Phthaleïns.*

Wool Book II.

*Basic Reds.*—

1. Rhodamine. Phthalein of diethyl-$m$-amido-phenol (basic hydrochloride). S. and J. 331.
2. Rhodamine B extra. As No. 1.
3. Rhodamine S. Succineïn of diethyl-$m$-amido-phenol-hydrochloride. S. and J. 333.
4. Rhodamine S extra. Succineïn of di-methyl-$m$-amido-phenol-hydrochloride. S. and J. 332.

### *Diphenylmethan Colours.*

10. Pyronin G. Tetra-methyl-diamido-oxy-diphenyl-carbinol hydrochloride. S. and J. 261.

### *Acridine Colours.*

5. Acridine red 3 B.

### *Azine Colours. Safranines.*

18. Magdala red. Diamido-naphthyl-naphthazonium chloride. S. and J.

### *Azo Colours.*

Wool Book I.

*Acid Reds.*—

12. Acid ponceau. From $\beta$-naphthylamine-mono-sulphonic acid and $\beta$-naphthol. S. and J. 92.
16. Double brilliant scarlet G. From $\beta$-naphthylamine-mono-sulphonic acid (Br.) and $\beta$-naphthol. S. and J. 94.

*50. Phenanthrene red.

54. Cresol red. From amido-ortho-cresol-ethyl ether and $\beta$-naphthol-di-sulphonic acid R. S. and J. 57.
58. Milling red G.
59. Clayton Cloth red. From dehydro thio-$p$-toluidine-sulphonic acid and $\beta$-naphthol. S. and J. 99.
60. Cloth red 3 G extra. From amido-azo-toluene and $\beta$-naphthylamine-mono-sulphonic acid Br. S. and J. 116.
61. Caroubier.
62. Fast red A. From naphthionic acid and $\beta$-naphthol. S. and J. 84.

*68. Fast red BT cmc. From $\alpha$-naphthylamine and $\beta$-naphthol-mono-sulphonic acid S. S. and J. 62.

73. Cloth red 3 B extra. From amido-azo-toluene and $\beta$-naphthylamine-mono-sulphonic acid S. S. and J. 115.

*76. Ponceau 2 S extra. From amido-azo-benzene and $\beta$-naphthol-di-sulphonic acid R. S. and J. 110.

83. Naphthorubin. From $\alpha$ naphthylamine and $\alpha$-naphthol-di-sulphonic acid. S. and J. 63.
84. Thiorubin. From dehydro-thio-$p$-toluidine and $\beta$-naphthol-di-sulphonic acid R. S. and J. 68.
88. Orchil substitute N. From $p$-nitraniline and $\alpha$-naphthylamine-disulphonic acid. S. and J. 39.
89. Bordeaux BX. From amido-azo-xylene and $\beta$-naphthol-$\beta$-mono-sulphonic acid. S. and J. 117.
90. Orchil substitute V. From $p$-nitraniline and naphthionic acid. S. and J. 36.
92. Milling red R.
94. Orchil substitute 3 VN. From $p$-nitraniline and $\alpha$-naphthylamine-mono-sulphonic acid L. S. and J. 38.
96. Fast red B. From $\alpha$-naphthylamine and $\beta$-naphthol-di-sulphonic acid R. S. and J. 65.

### *Natural Colouring Matters.*

Wool Book II.

*Acid Reds.*—

7. Lima-wood red (alumina mordant).
8. Lima-wood red (tin mordant).
9. Cam-wood red (alumina mordant).

NOTES.—The magentas are peculiar by becoming at first much bluer, so that at the end of the first "fading period" they appear somewhat darker; the purplish colour produced soon fades, however, and at the end of a year a pale grey remains. Acid magenta becomes duller but not bluer.

The rhodamines, Pyronin G, and Acridine Red become yellower.

Among the azo-colours those marked thus (*) are more fugitive than the rest. Cloth red 3 G extra and 3 B extra become distinctly yellower; ponceau 2 S extra becomes much bluer.

Cam-wood red is remarkable for becoming quite brown and appearing, therefore, darker at the end of the first fading period. This colour soon fades, however, and leaves at the end of a year a pale drab tint.

### CLASS III.—*Moderately Fast Colours.* (*Wool*).

The colours of this class show distinct fading at the end of the second period (June 14 to July 21, 1892), which becomes more pronounced at the end of the third period (July 21 to August 14, 1892). A pale tint only remains at the end of the fourth period (August 14 to February 16, 1893), and at the end of a year's exposure the colour has entirely faded, or, at most, mere traces of colour remain.

*Azo Colours.*

Wool Book I.

*Acid Reds.*—

3. Scarlet G. From xylidine and β-naphthol-di-sulphonic acid R. S. and J. 49.
4. Scarlet B.
5. Brilliant scarlet GG. From *m*-xylidine and β-naphthol-di-sulphonic acid R. S. and J. 50.
7. Lake scarlet GG. Same as 5.
10. Brilliant scarlet G. Same as 3.
11. Scarlet GR. From xylidine and β-naphthol-mono-sulphonic acid S. S. and J. 47.
14. Lake scarlet R. Same as 3.
15. Ponceau R.
17. Scarlet R. From *p*- and *m*-xylidine and β-naphthol-di-sulphonic acid R.
21. Scarlet 2 R. Same as 5.
22. Double brilliant scarlet 2 R.
23. Pyrotin red 3 RO.
25. Persian red.
27. Croceïn scarlet OXF. From naphthionic acid and β-naphthol-mono-sulphonic acid B. S. and J. 86.
28. Ponceau 2 R. From amido-azo-benzene and β-naphthol-mono-sulphonic acid B and S. S. and J. 108.
29. Cochineal scarlet 2 R. From toluidine and α-naphthol-mono-sulphonic acid C. S. and J. 40.
31. Cochineal scarlet 4 R. From xylidine and α-naphthol-mono-sulphonic acid C. S. and J. 45.
32. Ponceau 3 R. From amido-ethyl-dimethyl-benzene and β-naphthol-di-sulphonic acid R. S. and J. 51,
33. Coccin BB.
34. Naphthol scarlet.
37. Cochineal scarlet R.
38. Anisol red. From ortho-anisidine and β-naphthol-mono-sulphonic acid S. S. and J. 54.
39. Ponceau 4 R. From cumidine and β-naphthol-di-sulphonic acid R. S. and J. 51.
40. Azo-eosin. From ortho-anisidine and α-naphthol-mono-sulphonic acid NW. S. and J. 55.
41. Coccinin. From ortho-amido-phenetol and β-naphthol-di-sulphonic acid R. S. and J. 41.
42. Crystal ponceau. From α-naphthylamine and β-naphthol-di-sulphonic acid G. S. and J. 64.
49. Fast red E. From naphthionic acid and β-naphthol-mono-sulphonic acid S. S. and J. 87.
52. Cloth scarlet G.
64. Fast red C. From naphthionic acid and α-naphthol-mono-sulphonic acid NW. S. and J. 85.
66. Croceïn B. From amido-azo-benzene and α-naphthol-di-sulphonic acid Sch. S. and J. 107.
67. Cloth red G extra. From amido-azo-toluene and β-naphthol-mono-sulphonic acid S. S. and J. 113.
69. Bordeaux G. From amido-azo-toluene-mono-sulphonic acid and β-naphthol-mono-sulphonic acid S. S. and J. 126.
70. Orchil substitute G. From para-nitraniline and β-naphthylamine-mono-sulphonic acid Br. S. and J. 37.
71. Granat liquid.
72. Cloth red No. OG. Same as 67.
74. Cloth scarlet R.
75. Buffalo rubin. From α-naphthylamine and α-naphthol-di-sulphonic acid Sch. S. and J. 61.
77. Œnanthin. From naphthionic acid and naphthol-di-sulphonic acid.
79. Azo-red A. From amido-azo-naphthalene and α-naphthol-di-sulphonic acid.
80. Wool red.
81. Fast red D. From naphthionic acid and β-naphthol-di-sulphonic acid R. S. and J. 89.
86. Palatine red. From α-naphthylamine and naphthol-di-sulphonic acid. S. and J. 66.

*Induline Colours. Rosindulines.*

78. Rosinduline B.
82. Rosinduline BB.

*Natural Colouring Matters.*

Wool Book II.

*Acid Reds.*—

3. Cochineal crimson (alumina mordant).
4. Kermes crimson (alumina mordant).

### Class IV.—Fast Colours. (Wool).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth period a pale shade remains, which at the end of the year's exposure still leaves a pale tint.

*Azo Colours.*

Wool Book I.

*Acid Reds.*—

1. Ponceau 4 GB. From aniline and β-naphthol-mono-sulphonic acid S. S. and J. 27.
2. Ponceau 2 G. From aniline and β-naphthol-di-sulphonic acid R. S. and J. 29.
6. Ponceau RT. From toluidine and β-naphthol-di-sulphonic acid R. S. and J. 42.
8. Milling Red FGG. Constitution not published.
13. Wool Scarlet R. From xylidine and α-naphthol-di-sulphonic acid Sch. S. and J. 46.
18. Azo-coccin 2 R. From xylidine and α-naphthol-mono-sulphonic acid NW. S. and J. 44.
19. Brilliant Croceïn MOO. From amido-azo-benzene and β-naphthol-di-sulphonic acid γ. S. and J. 109.
20. Palatine Scarlet. From *m*-xylidine and naphthol-di-sulphonic acid. S. and J. 48.
24. Cotton Scarlet NT.
26. Crocein Scarlet 3 B. From amido-azo-benzene-mono-sulphonic acid and β-naphthol-mono-sulphonic acid B. S. and J. 120.
35. Double Brilliant Scarlet 3 R. From β-naphthylamine-sulphonic acid Br. and α-naphthol-mono-sulphonic acid NW. S. and J. 95.
36. Cochineal Red A. From naphthionic acid and β-naphthol-di-sulphonic acid G. S. and J. 88.
44. Fast Ponceau B. From amido-azo-benzene-di-sulphonic acid and β-naphthol. S. and J. 121.
45. Milling Red FR. Constitution not published.
46. Erythrin X. From amido-azo-benzene and β-naphthol-tri-sulphonic acid. S. and J. 111.
47. Crocein Scarlet 7 B. From amido-azo-toluene-mono-sulphonic acid and β-naphthol-mono-sulphonic acid B. S. and J. 125.
48. Ponceau S extra. From amido-azo-benzene-di-sulphonic acid and β-naphthol-di-sulphonic acid R. S. and J. 122.
51. Phœnix Red A. Constitution not published.
53. Cloth Red G. From amido-azo-benzene and α-naphthol-mono-sulphonic acid NW. S. and J. 106.
55. Ponceau 6 R. From naphthionic acid and β-naphthol-tri-sulphonic acid. S. and J. 90.
56. Coccinin B. From amido-*p*-cresol-methyl-ether and β-naphthol-di-sulphonic acid R. S. and J. 56.
57. Brilliant Crocein 9 B. Constitution not published.
63. Crocein AZ. From amido-azo-benzene and α-naphthol-di-sulphonic acid.
65. Erythrin P.
85. Crocein 3 B. From amido-azo-toluene and α-naphthol-di-sulphonic acid Sch. S. and J. 112.

(To be continued.)

## ON ERBIA.[*]

By GERHARD KRÜSS.

(Continued from p. 149).

### *Experimental Part.*

For the experiments there were used fractions rich in erbia which had been obtained from 5 kilos. of gadolinite earths by systematic precipitation of the total material with ammonia. The production of this material is given in *Liebig's Annalen*, cclxv., 10—12. The nitrate solution of the nitrate of these earths showed the erbium bands very intensely, but in a layer of 15 c.m. in thickness (a solution of 300 grms. nitrate in 150 grms. water) there was no trace of the didymium bands λ=579·2 and 575·4, which are generally very intense. This erbium material contained, as it is shown below, in addition to erbia other yttria earths. It was therefore first worked up by driving off the nitrates, and the nitrates were not, as it was sometimes formerly done, decomposed by heat so far as to give off red vapours of $NO_2$.

In the first place a smaller portion of this material was fused as nitrate, kept for some time in clear flux, and heated, with constant stirring, until the melt becomes turbid.

The cold melt was entirely soluble in water at the temperature of the room. The solution, however, when heated to 90° gave a crystalline deposit. This was filtered off, briefly washed with cold water, and yielded the first fraction; the filtrate of this separation was evaporated down, and the residue was treated in the same manner as the entire material had been. Thus there were obtained :—

Weaker bases ⟵. ⟶ Stronger bases.

| Fractions[†] | 1 | 2 | 3. | 4 | 5 | 6 | 7 (residue). |
|---|---|---|---|---|---|---|---|
| Series 1. $\overset{\text{III}}{R}$ = | 161 | — | — | — | — | 147 | 131 |

Fractions 1 to 4 were united, and from this material there was obtained the first relatively large separation[‡] of basic nitrate called *ytterbia* material (showing the Tm *α* line at λ=684 equally strong with Er *α*=654). The filtrate of this ytterbia material was added to fractions 5+6, and from this mixture the two first heavy precipitations (basic nitrate) were marked as "*Erbia material* No. 1," and the filtrate from these precipitations put back to fraction 7 (residue) as "*Yttria material*" after the above described manner of the partial decomposition of the earthy nitrates has been found practical, according to the spectrum of the several fractions. The main bulk of the erbiferous material was first worked up in a similar manner.

Weaker bases ⟵. ⟶ Stronger bases.

$$\begin{array}{lccccccccccccccc}
 & \multicolumn{9}{c}{\overbrace{\hphantom{1\quad 2\quad 3\quad 4\quad 5\quad 6\quad 7\quad 8\quad 9}}} & \multicolumn{6}{c}{\overbrace{\hphantom{10\quad 11\quad 12\quad 13\quad 14\quad 15}}} \\
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15\text{(res.)} \\
\text{Ser. 2.} & 165 & 62 & — & — & 162 & — & — & — & — & 149{\cdot}1 & — & — & — & — & 109{\cdot}7
\end{array}$$

*Spectroscopic Examination.*—Absent in the residue Tm *α*, which in Fraction 1 was equal to Er *α*. X *α* (holmium) increases in comparison to Er *α* towards Fraction 15 (residue).

There were first mixed together as—

A. Fraction 1, with 6 of second series, and ytterbia material from Series 1.
B. Fract. 7, with 14 of Series 2, and erbia material of Series 1.
C. Fract. 15 of Series 2 and yttria material of Series 1.

The present B material was characterised as erbia material No. 2.

There were then separated out as basic salts by heating the nitrates :—

A. Three precipitates—residue (strongest bases) to—
B. Of this the first heat-product (weaker bases) were added to A, six following nitrate fractions were kept separate as B, and the residue was added to—
C. Of the present C material, the first separation of basic nitrates was added to B, and of the entire B material now present, the first separation product was again added to A.

A was again resolved into fractions by heating the nitrates[*] :—

Weaker bases ⟵. ⟶ Stronger bases.

$$\text{Series 3.}\qquad \underbrace{1\qquad 2\qquad 3}_{171{\cdot}94}\qquad\qquad \underbrace{4\qquad 5\qquad 6}_{172{\cdot}6}$$

and the residue was added to A.

B. Eight fractions were separated :—

Weaker bases ⟵. ⟶ Stronger bases.

$$\text{Series 4.}\quad \underbrace{1\quad 2\quad 3\quad 4\quad\quad 5\quad 6\quad 7\quad 8}_{165{\cdot}9\dagger\qquad\qquad 163{\cdot}5}$$

and the earths which remained in solution after the last separation of basic nitrate.

C. This was the yttria material obtained from the yttria earths rich in erbia, as—
B. The fractions 1 to 8 of Series 4 were united, and were now marked as erbia material No. 3.

The few determinations of equivalents were merely executed for accessory orientation.

A. Fraction 1 to 6 of Series 3 now formed the ytterbia material.

These three materials were further decomposed by precipitation with aniline in alcoholic solution, as described elsewhere by the author.

(To be continued.)

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## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.[‡]

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 133).

The case is not distinguished in form and arrangement from the ordinary wooden cases. It has a slide and a cover like these, and it can also be displaced for the reception of spectra placed below each other in the direction of the spectral lines according to a scale applied laterally, so that a plate with a sufficiently short slit-aperture may serve for a great number of proofs. The internal surfaces of the camera and of the cases, as the glass of which they are made is transparent, have a thin lining of a dead black colour. The outside is coated with black paper and shellac varnish. The size of the plates is 30 by 65 m.m.

I have used glass for the camera in preference to wood, because, notwithstanding the requisite—and perhaps little trustworthy—paper coating, it is not greatly suscep-

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[*] *Zeitschrift fur Anorganische Chemie.*

[†] For the sake of brevity the results of the determinations of equivalents carried out as a preliminary on the earths of the several fractions are given in the sequel solely in the form of tables, the triple equivalent being placed beneath the number of the fractions. The quantity of the $\overset{\text{III}}{R}$ found is a measure for the Sc, Yb, Tm, Er, Ho, Tr, and Y.

[‡] The quantity of the separation may be increased if, after heating the dissolved melt the solution is evaporated down and heated again.

[*] It was again heated until the melt became turbid. The product was soluble in cold water, and their solution when heated gave a precipitate which was at first soluble and then became crystalline.

[†] The nitrate melt of B was soluble in hot water, but the solution on cooling deposited a strongly red crystalline precipitate=Fract. 1, Series 4.

[‡] From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

tible to the changes of atmospheric heat and moisture, and because wooden cases for such small plates can scarcely be made more accurately than those of glass. During use extending for months the glass camera has never given occasion for dissatisfaction.

### *Setting up the Spectral Apparatus and the Auxiliary Plant.*

The source of light must be adjusted with the aid of a telescope. In order to keep the telescope and the collimator as much as possible co-axial during the duration of the entire experiment, a foundation was required as little sensitive as possible to atmospheric influences. For this purpose also I selected glass. A quadrilateral disc of mirror-glass with sides of 1 metre in length and 10 m.m. in thickness was fixed upon a very stable wooden foundation in such a manner that it was supported only in some few points. The position of the supports was selected so that the changes to which the wooden foundation was liable could be conveyed to the direction of the apparatus only in a very reduced proportion.

The apparatus directly concerned in obtaining the proofs was set up on the glass plate as follows, and, where practicable, it was especially secured against lateral displacement:—

Opposite to the spectroscope, and co-axially with the collimator, stood the reading telescope; between both, the spark-support; and close before the slit, a second stand with a slit-shaped screen of adjustible length. Between the spark-stand and the screen there was placed, for a portion of the proofs, a condenser, of which more below. The screen came into use if the aperture of the slit was to be opened to the rays only for a part of its length. It could also be displaced along the slit by means of rack-work in the support, so that the slit could be opened at any point to the length desired, and, if necessary, also in an uninterrupted succession at the transitions. The screen, as well as the sparks, required the reading-telescope for accurate adjustment. This will be more intelligible if I add that the aperture of the slit-length moved within very narrow limits, and often did not exceed the modest measure of 0·2 m.m., and that, on the other hand, the sparks and the screen were generally at the distance of some centimetres.

### *The Source of Light.*

The primary current was supplied by a chromic acid battery of four large immersion elements. Besides the inductorium (formerly used) of 25 c.m. spark-length and the Leyden jars, there were also used this time a smaller inductorium for sparks of only 8 c.m. in length. In some cases the inductorium was exchanged for an induction machine (four pairs of discs of 62 and 70 c.m. diameter) connected with a Riess's jar-battery (nine Leyden jars with an external coating of 1¼ metres).

As electrodes there were again used temporarily cadmium and zinc; afterwards, permanently, aluminium, and finally, Ag, As, Au, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mo, Na, Ni, Pb, Pd, Pt, Sb, Si, Sn, Tl, W, all in the state of wire or short rods (Ca, K, Na, W), or crystals (Si), which were held in clamps of copper or platinum.

### *The Photographic Process.*

This time also, when the utmost sharpness of design was needful, plates of my own preparation were used. But in general the photos were obtained upon plates by Herrn E. Zettnow. In all cases I preferred them to my own plates, on account of their great sensitiveness and intensity, except where the utmost sharpness of the spectral lines was essential. Some spectra were taken upon Schleussner plates. The Schleussner plate works also clear and is very sensitive, but its negatives betrayed the above-mentioned defect of all commercial plates—they were wanting in the intensity required for taking spectra. The developer and the fixing agent consisted, as formerly, of pyro-soda and sodium thiosulphate.

The number of the negatives thus obtained is relatively large. The author's diary gives a conscientious account of the conditions under which each proof was taken. Every plate, even if a failure, is given in the order of time, and with a progressive number and the negative bases have the same number.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

The following is the text of the Address presented to Sir John Lawes, Bart, &c., and Dr. Gilbert, on July 29th, on the occasion of the Rothamsted Jubilee:—

We, the President and Officers of the Chemical Society of London, on behalf of the Council and Fellows generally, desire on this occasion to express our sense of the extraordinary value of your labours in the field of agricultural science, our admiration of your researches, and our gratitude for the immense number of exact data which you have placed at the disposal of chemists.

Few men have been able to conduct experimental researches during so long a period, and there is no parallel in the history of science to your achievement in carrying on a single research without interruption during a period of over fifty years. The plan laid down at its commencement has throughout been most rigidly adhered to, which is evidence of the skill originally displayed in its inception, and gives to your work its pecular value.

While affording guidance to the agriculturist, your researches have elicited information which will ever serve as the foundation of a truly scientific knowledge of the correlation of plant growth and manurial constituents of the soil, and will be of the utmost value in all discussions of the chemistry of plant life. Your researches on the feeding of animals, in like manner, are not only of practical importance, but also shed much light on the processes of animal life.

Great, however, as is the actual value to agriculture and agricultural science of your work, the example your single-minded devotion to the cause of scientific truth and research has afforded to the world is unquestionably to be regarded as of far greater value. Yours is the model of all agricultural experimental stations, and the methods that you have introduced are everywhere regarded as classical.

The rare and enlightened munificence which has led the one of you to institute and maintain such a series of enquiries having been supplemented by a provision for the future conduct of the experiments in order especially to make it possible to deal with the great question of the ultimate exhaustion of the soil, the debt of gratitude which science owes to the founder of the Rothamsted experimental station is extended into the distant future.

It is, consequently, with a full sense of the inadequacy of our expressions that we to-day offer to you our heartfelt thanks and our warmest congratulations on your having been able to achieve results of such magnitude and importance.

**The Birkbeck Institution.**—The Committee of the Birkbeck Institution, adopting the principles laid down in the Report of the London County Council on Technical Education, purpose appointing a Professor of Chemistry who shall devote his whole time to the work, including practice in original research. Mr. Chaloner, who has had charge of the Inorganic Classes for the last twenty-five years, will accordingly shortly retire.

## CORRESPONDENCE.

### THE INSTITUTE OF CHEMISTRY.

*To the Editor of the Chemical News.*

Sir,—Now that we members of the Institute of Chemistry are last in the proud position of having a house of our own in London, may I ask through your columns whether the Council propose making any use of it, or whether they intend keeping it simply for ornament?

It seems that there are a number of rooms (five or six), I understand, which will not be required for office and other accommodation, and an idea has got abroad that they might be used as the head-quarters of a chemical club. Can we not persuade the authorities to take up this idea, and furnish the rooms so that they might be available for this purpose, and also as a place where Fellows—especially the country ones—could meet their clients for consultations, or even pass the night during their visits to London? If this suggestion were taken up, there is little doubt that the town members would gladly pay a small local subscription for the convenience; and to the country men the Institute would become something more than a name—high-sounding, it is true—but still perilously near being an empty one.—I am, &c.,

An East-End Londoner.

September 20, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 10, September 4, 1893.

This issue contains no chemical matter.

No. 11.

**Presence of a Ferment Analogous to Emulsine in Fungi, and Especially in Fungi Parasitic on Trees and Living on Wood.**—Em. Bourquelot.—The author finds that many fungi contain a ferment capable of splitting up various glucosides, such as amygdaline, salicine, and coniferine. It acts in the same manner as the emulsine of almonds. The author enumerates the species in which he has proved the presence of a ferment.

**A Method of Determining the Density of Gases Applicable in Industry.**— Maurice Meslans.— This paper does not admit of useful abstraction.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 90.

This number contains no chemical matter.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., Nos. 15 and 16.

**Precipitation of Manganese by Oxygenated Water and Ammonia, for its Determination, Gravimetric or Volumetric.**—Adolphe Carnot.—This paper will be inserted in full.

**Carbohydrates of the Jerusalem Artichoke.**—Ch. Tanret.—The carbohydrates present in the juice of the *Helianthus tuberosus* are—Inuline, pseudo-inuline, inulonine, helianthenine, synanthrine, saccharose, levulose, and glucose. Of these substances synanthrine is the most abundant. For separating these substances the author first treats the juice of the tubers in heat with basic lead acetate, removes excess of lead with dilute sulphuric acid, and adds a large excess of concentrated baryta water. He then precipitates all the carbohydrates with alcohol at 90°. He decomposes the precipitate with $CO_2$, boils, filters, and evaporates to dryness. The residue treated with boiling alcohol at 84° gives up the helianthenine, of which only 1-300th part remains in the liquid. The insoluble residue is then treated with boiling alcohol at 70°, which takes up the inulenine. The residue contains merely pseudo-inuline and inuline, which are separated by treatment with 10 parts of boiling alcohol at 60°. The pseudo-inuline dissolves and the inuline remains undissolved.

**On Calcium Oxyiodide.**—M. Tassilly.—The compound obtained has the composition $CaI_2,3CaO,16H_2O$, corresponding to the oxychloride studied by André.

**The Reaction of Ethyl Bromo-propionate and Sodium Nitrite.**—G. Lepercq.—The crystalline compound obtained, $C_5H_9NO_3$, is probably the ethyl nitroso-propionate obtained by V. Meyer and Züblin by the action of nitrous acid upon methyl-acetylacetic ether (*Berichte*, 1878, p. 693).

## MISCELLANEOUS.

**Chicago Exhibition, 1893.**—The following description of the platinum, precious metals, and manufactures exhibited by Johnson, Matthey, and Co., will be read with interest:—

*Platinum Apparatus of the Most Improved Form, "Double Delplace," for Concentration of Sulphuric Acid.*—This apparatus is capable of concentrating 22,000 lbs. O. V. 94 per cent per twenty-four hours under ordinary working conditions, and about one-half this quantity of 97½ per cent $H_2SO_4$. It is the most universally adopted and approved form of apparatus, and some hundreds have been supplied throughout the world by Johnson, Matthey, and Co., since its introduction by them in the year 1875. It is a form which assures the greatest productive power, economy, and regularity in working, and can be adjusted to produce any strength of acid required up to the maximum 97/98 per cent $H_2SO_4$.

*Gold-Lined Platinum Apparatus for the Concentration of Sulphuric Acid, Manufactured by Johnson, Matthey, and Co.'s Process of* 1854.—(Platinum 75 per cent, gold 25 per cent).—The gold surface is alloyed with 5 per cent platinum to give the necessary hardness and durability. This alloy has been proved by the most careful tests as to wear and tear under working conditions at highest pressure to be subject to only one-half the loss of that of pure gold. A large boiler so manufactured was exhibited by Johnson, Matthey, and Co. in the Paris Exhibition, 1855, as shown by the annexed extract from Mr. Alfred Tylor's "Report on the Paris Exhibition, 1855, on Metal Work," p. 275, Part 2. Published by Eyre and Spottiswoode for Her Majesty's Commissioners, 1856. "Johnson and Matthey exhibit a retort of a different form to any previously used, and which they say has been highly approved by a sulphuric acid maker, who is now working a similar one. They state that after fifteen or twenty years, platinum by use loses one-fifth of its weight, probably from the action of impurities in the acids boiled in it, and requires frequent repairs with gold solder. They observed that these patches of gold were perfectly untouched, and have therefore *welded* an ingot of gold upon the platinum, so that, when manufactured, the interior of the pan should have a surface of gold."

*International Standard Metre and Kilo.*—Platinum 90 per cent, Iridium 10 per cent, Density 21·552).—This alloy, finally adopted after long experiment by the Paris International Commission, was recommended by Johnson, Matthey, and Co., and shown by them at the Vienna Exhibition, 1873, and all the standard metres and kilos. for international use have been subsequently prepared and supplied by them of this alloy and form to the International Committee of Weights and Measures, the experts appointed by whom to determine the quality of the platinum employed (the most distinguished *savants* in this branch of metallurgy—M. H. St. Claire Deville and M. Debray, of Paris, and M. Stas, of Brussels) reported its purity = 999·98773 per 1000, a degree of purity heretofore (1873) considered commercially impossible, and, except by their special process, even now only attainable in laboratory experiments of a very costly nature and dealing with small quantities. The weight of platinum employed in the manufacture of these standards was 250 kilos. (about 8000 ounces troy). The preparation of so large a quantity of platinum to the above high degree of purity is considered by scientists to be unsurpassed in metallurgical annals.

Metre Tubes in Iridio Platinum—for measuring the coefficient of expansion of the international geodesic rule and thermometric metre, prepared specially for experimental work carried out at the Eçole Normale, Paris.

Platinum Basins and Crucibles Gold-Lined, 10 per cent to 25 per cent—Gold.

Platinum ann Iridio-Platinum Crucibles, Dishes, and Capsules—for laboratory use.

Platinum Apparatus for the Evaporation of Liquids by Heat, Generated by Electricity—consisting of a platinum rectangular pan, fitted interiorly with insulators, holding the necessary platinum heaters.

Specimens of the Autogenous Soldering of Platinum—a process introduced by Johnson, Matthey, and Co. in 1859, and subsequently adopted for all important work.

Series of Iridio-Rhodio-Platinum Alloys—sheet and wire, for electrical, technical, and scientific purposes, proportions varying from 3 per cent to 20 per cent. These very interesting compound alloys merit special attention.

Wire shown in gradations of ordinary sizes for dental, electrical, technical, and scientific uses:—

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Pure Iridio Platinum Wire.
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*Pure Metals of the Platinum Group.*—Ingot of Pure Palladium, 1000 ozs., value £7000, extracted from gold and platinum of the value of about £2,250,000. Pure Melted Iridium, weight 240 ozs., value £1500. Pure Melted Ruthenium. Pure Melted Rhodium. Pure Melted Osmium. Pure Metallic Osmium, crystalline.

A Series of Oxides, Salts, and Compounds of Ruthenium.

Specimen of Silk Dyed with Ruthenium.
Pure Crystalline Boron and Silicon.

Aluminium Coins—hardened with 2 to 10 per cent of nickel. The alloy prepared and recommended for coinage purposes by Johnson, Matthey, and Co. in 1878.

**An Irreverent Practical Joke.** — According to an eminent medical contemporary, at the celebration of the birthday of the Emperor Francis Joseph some irreverent joker introduced a quantity of silver nitrate into the holy-water recipients at Trieste Cathedral. The effect upon the fingers and faces of the faithful may easily be imagined.

**The Composition of the Moon.**—Among a number of books advertised by an eminent Hamburg publishing firm we find a pamphlet from the pen of "Dr. Mises" (apparently a pseudonym for G. Th. Fechner) proving that the moon is composed of iodine. Perhaps in time the renowned green cheese theory may yet be demonstrated. In another pamphlet the same author contends that shadows are alive, and that the world has been produced, not by a primal creative, but by a destroying principle.

**Mr. C. Watson Smith.**—A copy of the Address given in University College, London, during last winter, on the "Diseases Incident to Workpeople in Chemical and other Industries," by Mr. Watson Smith, has been recently forwarded by him, along with a letter, to the Emperor of Germany, who, as is well known, takes a lively interest in the welfare of the workpeople of his realm. The following graceful acknowledgment has just been received by Mr. Watson Smith:—"The German Ambassador presents his compliments to Mr. Watson Smith, and has the honour to inform him that the copy of his treatise on diseases of occupation in connection with chemical industries, which he offered for the acceptance of His Majesty the Emperor, has been accepted by His Majesty. By command of the Emperor, the Ambassador begs to convey to Mr. W. Smith his thanks for the kind attention shown to him. —German Embassy, London, Sept. 16, 1893."

**Proposals for Standardising in Acidimetry and Alkalimetry.**—E. Brentel (*Oest. Chem. Gesellschaft* and *Zeit. Anorganische Chemie*) recommends potassium bichromate as the starting-point for acidimetry. It is heated to fusion, weighed when cold, and the titration is effected with baryta water, using phenolphthalein as indicator. E. Rimbach (*Berichte*), in the course of his studies on the atomic weight of boron, has satisfied himself that the soda in borax can be very sharply titrated with hydrochloric acid, using methyl orange as indicator. As borax can be obtained sufficiently pure for ordinary purposes by re-crystallisation and exposure to the air, he proposes to use it instead of sodium carbonate for determining acids. 1 grm. of crystalline borax weighed in air with brass weights corresponds to 5·2391 c.c. normal acid. Hence 1 litre normal acid equals 190·872 grms. borax. Th. Salzer (*Berichte*) states that he made the same proposal some time ago, and it is consequently found in the second edition of "Mohr's Text-book of the Volumetric Method. In a second paper (*Pharm. Centralhalle*) Salzer discusses the question what indicator should be selected when using borax, and shows that the methyl orange preferred by Joly and Rimbach is preferable to litmus only in concentrated solutions, but that it is less sensitive in dilute liquids. The author recommends the use of a decinormal solution, with litmus as indicator, titrating from an onion-red to a bluish red. M. Weinig (*Zeit. Angew. Chemie*) recommends, whilst considering the gravimetric standardising of sulphuric acid, besides precipitation with barium chloride and standardising with sodium carbonate, the two following methods:—1. Of two equal portions of sulphuric acid, the one is titrated with baryta water and into the other is distilled ammonia evolved from a solution of ammonium chloride of known strength, the residue of the sulphuric acid being again titrated with baryta water. The standard of the sulphuric acid may be calculated from the result. 2. The method recommended by Schaffgotsch for the determination of nitric acid, *i.e.*, evaporation with an excess of ammonia, is also applicable for sulphuric acid. A known quantity of sulphuric acid is put in a platinum capsule along with a slight excess of ammonia (about 0·5 c.c. more than requisite for neutralisation), evaporated to dryness, dried for half an hour at from 115° to 120°, and weighed. This proposal has been tested by H. Eckenroth (*Pharm. Zeitung*), and found very convenient, as also for hydrochloric and oxalic acids.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Etching Glass.**—Will any reader kindly tell me where to get information relative to the practical working of etching glass by fluorine compounds?—C. M. Silverburn.

## TO CORRESPONDENTS.

*Edouard.*—We should recommend a year at the Royal School of Mines. Obtain the books there in use.

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THE CHEMICAL NEWS.

Vol. LXVII., No. 1767.

## ON THE OCCURRENCE OF CYANO-NITRIDE OF TITANIUM IN FERRO-MANGANESE.[*]

By T. W. HOGG.

In this paper is given a short account of the fact that there are probably about half a million isolated crystals of cyano-nitride of titanium in each cubic inch of the high percentage ferro-manganese now used for steel-making purposes, titanium carbide and nitride being also occasionally present. The size of these crystals generally lies between 1-10,000th and 1-1000th of an inch, comparatively few of them being greater than this.

The number of crystals has been counted, and the lowest estimate gave 336,000 to the cubic inch of alloy; as a matter of interest the weight of this number of cubes of cyano-nitride of titanium of 1-10,000th of an inch has been calculated, and found to be only 0·00003 of a gramme; similarly the weight of the same number of cubes of 1-1000th of an inch weigh 0·03 grm. The crystals are possessed of a high metallic lustre, with brilliant mirror-like facets, and occur in the form of cubes, octahedra, and forms resembling the icositetrahedron; there are also present beautiful combinations of prisms and pyramids, and many of the cubes have interesting symmetrical face modifications. As these different forms are all found together, they are microscopic objects of great beauty and interest to the student of crystallography.

These crystals are obtained by careful elutriation of the carbonaceous residue left after treating considerable quantities of the ferro-manganese with hydrochloric acid, cupric chloride, or dilute nitric acid. This latter is recommended as being the most convenient; in using it the mixture is kept as cold as possible, and allowed to stand for about twenty-four hours; the large crystals separate at once, the smaller forms being retained in the residue, which must be dried and gently pounded before submitting it to elutriation: this is best performed in a large porcelain basin, using plenty of water and gently rocking and rotating the mixture, and allowing it to rest at intervals; the lighter portions are then sucked up by means of a pipette, this being continued until nothing but the copper-coloured crystals are left.

The largest quantity which has been separated in this way is equal to 0·032 per cent.

Ferro-manganese containing different percentages of manganese and of different makes has been examined, and, with the exception of spiegeleisen containing 11 per cent Mn, they have all been found to contain this remarkable compound.

As the quantities available for examination are only small, with the exception of specific gravity and the titanium, only qualitative tests have been applied. In different specimens the sp. gr. has been found to vary between 4·1 and 5·1, and the titanium from 60·5 to 79·8 per cent. These latter determinations include a small proportion of iron, which has always been found to be present: this is also the case with crystals separated from an old blast furnace "bear"; after several days heating with hydrochloric acid there is still 1·5 per cent of iron retained, and probably this is the cause of the crystals being slightly but distinctly magnetic.

Attention is especially directed to the fact that much valuable information with regard to the condition of the foreign elements may be obtained by decomposing large quantities of the alloys with suitable reagents, and separating the substances of different specific gravity from the residue: in doing this it is pointed out that there is great danger of decomposing the compounds originally present, and forming new ones as a result of the reaction which takes place between the reagent and the various substances present. Such a method as is indicated in this paper is recommended to be used in conjunction with the examination of etched specimens. which of themselves do little beyond revealing changes of structure induced by different modes of manipulation and varying temperatures; the insufficiency of etched specimens to give us information with regard to the condition of impurities is evident from the fact "that, being opaque, so nearly alike in colour, and in such minute and uniformly distributed particles, they escape observation."

## THE CAUSE OF THE RED COLOURATION OF PHENOL.[*]

By CHARLES A. KOHN, Ph.D., B.Sc.,
Lecturer on Organic Chemistry, University College, Liverpool.

The cause of the turning red of phenol has from time to time been the subject of investigation, but the published results are both vague and conflicting. Whilst the balance of opinion has favoured the view that the colouration is to be traced to some impurity—generally metallic—present in the phenol, others have traced the colouration to the presence of cresol, which in combination with phenol is supposed to give rise to the formation of rosolic acid. More recently, Fabini has stated that the colour formed is produced by the combined action of hydrogen peroxide, metallic salts, and ammonia, and that all three reagents must be simultaneously present for the colouration to ensue.

Since alkalis (especially ammonia), metallic salts, and oxidising agents play an important part in the turning red of phenol, their separate and combined actions on specially purified phenol has been investigated. The purest commercial phenol, known as "absolute phenol," was used in a portion of the experiments; in the remainder, a specially purified sample, kindly prepared by C. Lowe, Esq., of Manchester.

This phenol was first purified by repeated distillation from glass vessels, the first and last portions of each distillate being rejected. The distilled product was then tested with hydrogen peroxide, ammonia, caustic potash, iron and copper salts, after one, six, nine, and fifteen distillations respectively.

The tests were carried out by placing 2—3 c.c. or the melted phenol in a test-tube and adding one of two drops of the reagent or mixtures of the reagents. The reagents were employed in various strengths.

Under all conditions a colouration was found to result, even with the fifteen-times distilled product, whilst comparative tests showed that no further purification had been effected after the second distillation. Ammonia in concentrated solution produces a deep blue colouration, identical with Phipson's "phenol blue," and probably the same product as phenol-quinone-imide. The formation of this colour has long been known, and seems to have been quite overlooked by Fabini in his statement that, in addition to ammonia, metallic salts and hydrogen peroxide are also necessary for a colouration to be formed. Very dilute ammonia, in common with hydrogen peroxide, caustic potash, hydrogen peroxide in presence of ammonia, or of caustic alkali, metals, or metallic salts, with or without hydrogen peroxide, produces a reddish

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[*] Read before the British Association (Section B), Nottingham Meeting, 1893.

[*] Abstract of a Paper read before the British Association (Section B), Nottingham Meeting, 1893.

colouration. The intensity and tint of the colours produced by these different reagents vary considerably, but in most instances it inclines to red—the colour usually formed in commercial phenol. Whilst it is not likely that these colours are identical, it is probable that they are closely allied products, and the conditions of their formation point to their being oxidation products of phenol. Gentle heating in all cases aids the formation of these colourations.

The phenol, both after nine and after fifteen distillations, was carefully tested for metallic impurities and was found to be quite free from the same. Further, in order to test whether iron and copper salts were readily carried over by phenol when distilled, the product was distilled after the addition of these metals and of their salts, with the result that after two careful distillations from glass vessels the distillate was found quite free from metallic contamination.

That *pure* phenol behaves as described with the above reagents was confirmed by applying the same tests to phenol purified by sublimation, and also to that obtained by the saponification and subsequent decomposition of gaultheria oil.

The incorrectness of Fabini's view of the cause of the colouration was thus fully confirmed. The complete concordance in the behaviour of the phenol prepared from such different sources, and purified by different methods, shows that the re-distilled "absolute" phenol is in reality a pure product, and that the colour reactions observed with it are not to be traced to the presence of hidden impurities.

Of greater importance than the action of these various reagents upon purified phenol, is the fact that the pure product obtained by each of the above processes does of itself become coloured when exposed to ordinary moist air. The colouration, which gradually deepens from pale pink or brown to red, is always accompanied by the absorption of moisture, and the reddening is especially conspicuous in the partially liquefied parts of the sample. This colouration does not take place in the dark, nor under red glass; it is the work of the more refrangible rays of light only.

As has often been observed, sublimed phenol does not redden as rapidly as the distilled product; in fact, according to Bidet, it does not colour at all on exposure when thus purified. This, however, is not the case, the sublimed product becomes coloured quite as quickly as distilled phenol when in solution, and that it is slower in turning pink when in the solid state is due to the fact that the crystals obtained by sublimation are less hygroscopic than the distilled product. In absence of moisture, under all conditions, no colouration ensues; hence the appearance of the colour in those portions of the sample which have become partially liquefied. Phenol placed *in vacuo* can be exposed to light for months without becoming red, nor does it colour either in presence of moisture when air is absent, or in presence of air when perfectly dry. Both air and moisture are necessary for the colouration to take place.

The similarity between the coloured product formed by the action of moist air and phenol and that produced by hydrogen peroxide naturally led one to look to the latter as the real factor in the oxidation. That such is the case has been conclusively shown by Dr. A. Richardson, who has succeeded in detecting the presence of hydrogen peroxide in reddened phenol, both by the chromic acid and by the titanic acid test.

Dr. Richardson very kindly communicated his results to me, as I had myself not succeeded in detecting the presence of this body with certainty; a fact due, as I subsequently ascertained, to the exposures having been made under conditions in which the hydrogen peroxide formed was used up for the oxidation of the phenol as rapidly as it was produced. Dr. Richardson further ascertained that the blue rays of light and not the red are the active agents in the production of hydrogen peroxide when phenol is exposed; a fact which further emphasises the relation of its formation to the colouration.

This same colour is produced, together with a complexity of other substances, when phenol is electrolysed in acid solution. The nature of the coloured product formed is still under investigation, and not until the colouring-matter itself is more completely studied can any conclusion be drawn as to the course of the oxidation. Meanwhile the fact that phenol, when perfectly pure, does possess the intrinsic power of turning red when exposed to ordinary moist air is of some technical importance, and points to the futility of the numerous processes proposed for preventing such colouration, as well as to the conditions under which the product can be best prepared and kept so as to impede the formation of the colour.

# ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 159).

### *The Photographic Proof.*

The commencement of my proofs fulfilled my expectations only to a very modest extent. My apparatus, indeed, as it was to be expected from the size of its aperture, was found very light-proof: but the two most refrangible rays of cadmium, Nos. 25 and 26, contrary to my anticipation, had gained little in intensity. It was not much better with the most refrangible lines of zinc, Nos. 27, 28, and 29. They certainly appeared earlier than previously, but their intensity still decreased decidedly with their wave-length. Hence it seemed as if the suspected action of the atmosphere might chiefly be reduced to a specific property of the lines concerned. But even this, as it appeared in the course of my subsequent researches, was in part correct; the main difficulty in my earlier proofs of the most refrangible rays lay in the imperviousness of the air to light. This resulted clearly from the proof of the aluminium spectrum which next followed. All the main lines appeared in a few minutes, and in greater intensity than heretofore. The most refrangible—the double line, No. 32—acted now always first, in contradistinction to former results, and its components were of equal strength, a circumstance which I emphasize merely because it acquired especial importance for certain subsequent proofs. Next to it there appeared the least refracted line, No. 30, and only some time after the intermediate line, No. 31, the least refracted component always first. On brief exposure the more strongly refracted component did not appear at all, and even on prolonged exposure it remained far behind all the other lines.

This behaviour of the aluminium spectrum with the new apparatus ensued whether the proof was taken with or without a condenser, and with plates of high or low sensitiveness. In contrast to earlier observations the lines, after an exposure of three minutes, displayed an intensity and distinctness quite sufficient for the purpose of measurement.

On more prolonged exposure the more effective lines acquired the greatest intensity which the gelatin plate admits of. But very remarkably the action of light in this reagent is confined to these rays, whilst the less deflected portion of the ultra-violet is distinguished by an exactly opposite phenomenon,—the access of new lines and their growth to a continuous band of the deepest blackness. Owing to this circumstance the proofs have a

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

peculiar appearance: they produce the impression as if the activity of their most refrangible half were still checked by some hindrance. We are compelled to this conclusion by the great intensity of lines No. 32, with which the effective band of the aluminium spark in the ultra-violet suddenly ends, and whereby, at the same time, the assumption of its prolongation towards the more refrangible side, where hitherto no action of light has been observed, receives a certain justification. It was this consideration which led my work from the path of reproductivity, on which it had hitherto mainly moved, towards new facts.

My endeavours were henceforth directed to bring into photographic activity the region between the lines Nos. 30 and 32, which hitherto, with the exception of line No. 31, had evinced no reaction to light whether in my hands or in those of other experimenters. I sought to effect this, in the first place, without reference to graphic completeness, proceeding on the assumption that the previous want of success was due not to the absence of all radiation, but to the imperfection of the method of observation.

I first strengthened the illumination with energetic short sparks, springing over close in front of the widely-open slit, and, with the lenses fully open, I obtained on a Zettnow plate, after exposure for half an hour between the components of the line No. 32, first two marked lines, then—on prolonged exposure on both sides of the same line—a band of action composed of dense groups, which continually extended further with the increase of the illumination.

On an exposure of an hour and a half the entire aluminium spectrum consisted of an almost continuous band, which ended only beyond the previous boundary of the ultra-violet, about at the wave-length 183 $\mu\mu$. That we have here to do with the spectrum itself, and not with an action of diffused light, was shown by the fluctuating intensities and the marked lines by which the newly-acquired region is distinguished. In how far this is to be ascribed to the aluminium or to its impurities, or to the atmosphere, I must leave an open question. But for me a more important consideration was the fact now ascertained, that the region between the main lines of aluminium and a slight distance beyond, though hitherto regarded as void of light, displayed a quite unexpected wealth of rays.

Such being the case it was to be expected that not aluminium alone, but other substances, would admit rays of such strong refrangibility. This conjecture was actually confirmed when I submitted a series of elements to examination.

I adduce below these spectra in chronological order. In place of a photographic reproduction, which I reserve for a future occasion, I give the main data of the experimental arrangement and the photographic result, in order to furnish some basis as to the energy and the number of the new lines, in as far as they lie beyond the wave-length 188·8 $\mu\mu$.

(To be continued.)

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## ON ERBIA.*

By GERHARD KRÜSS.

(Continued from p. 158).

### *The Ytterbia Material.*

Weaker bases ⟵. ⟶ Stronger bases.

| Series 5. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 (residue). |
|---|---|---|---|---|---|---|---|---|---|
| | 173·6 | 175·5 | — | 172·5 | — | — | 173·4 | 174·6 | 172·5 |

*Colour of Oxides.*—White from 1 to 7; from fraction 8 onwards, distinctly reddish.

*Spectrum of the Earth Solutions.*—1 to 7 without bands. Fractions 8 and 9 showed faint Tm and Er lines. For a general view to ascertain whether the feebly basic scandia was present in the ytterbia material, the fractions 1 and 2 were mixed and about one-fourth was precipitated with aniline, $\overset{\text{III}}{\text{R}}$ of this precipitation = 173·2, whence scandia is probably absent.

### *Erbia Material No. 3.*

### *Series 7.*

Weaker bases ⟵.

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| 148·0 | — | 139·8 | 140·5 | — | 142·3 |

⟶ Stronger bases.

| 7 | 8 | 9 | 10 | 11 | 12 (residue). |
|---|---|---|---|---|---|
| 135·8 | 125·7 | — | — | 115·4 | 93·9 |

*Colour of the Oxides.*—Deep yellow up to the residue, which is nearly white.

*Spectrum.*—Chiefly X lines, which become very faint towards the end of the series.

According to P. Cleve, on fractionating ytterbia-erbia earths, nearly colourless earths are obtained as fractions of mean basicity; the spectrum of which contains chiefly an absorption band at $\lambda = 684$. Cleve found the $\overset{\text{III}}{\text{R}}$ resulting from the equivalent of these earths situate between the values of ytterbium and erbium, $\overset{\text{III}}{\text{Yb}} = 173$ $\overset{\text{III}}{\text{Er}} = 166$, and inferred hence the existence of a substance which he named thulium, $\overset{\text{III}}{\text{Tm}} = 171$. The above experiments fully confirm those phenomena first observed by Cleve; which, however, do not contain any binding proof that we have here an unitary earth corresponding to $\overset{\text{III}}{\text{R}} = 171$. To this point we shall return in a subsequent memoir. In the meantime, the earths corresponding to Cleve's thulia were united as—

### *Thulia Material.*

*Series* 5, Fraction 9, ytterbia material; and
*Series* 6, Fractions 1, 2 and 3, erbia material.

The first precipitate from this with aniline in an alcoholic solution was returned to the total ytterbia earth, Series 5, and the rest was further decomposed in the same manner.

### *Thulia Material.*

Weaker bases ⟵. ⟶ Stronger bases.

| Series 8. | 1 | 2 | 3 | 4 | 5 (residue). |
|---|---|---|---|---|---|
| | 171·6 | — | — | 157·5 | 156 |

After the erbiferous yttria earths originally taken in hand, as shown in the Series 5—8, had been decomposed, those fractions were selected for preparing the true erbia earth which, (1) according to their position in the above series, contained earths rather more basic than those present in the thulia material. (2) Those which in the determination of their equivalents gave values of about 166 for $\overset{\text{III}}{\text{R}}$; and (3) those which on analysis certainly yielded values rather lower than Er = 166, but which, according to their position in the series, contained along with holmia, terbia and yttria; and, according to the spectroscopic examination, contained erbia in quantity.

Hence there were united as the present *Erbia Material No.* 4—

*Series* 6, Fracts. 4 to 9 inclusive, erbia material; and
*Series* 7, Fraction 1, yttria material.

These earths in an alcoholic solution of their chlorides were partially precipitated with aniline, and yielded—

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* *Zeitschrift fur Anorganische Chemie.*

Feebler bases ←—. —→ Stronger bases.

| Series 9. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| | 172·4 | 168·8 | 167·7 | 165·9 | 158·5 | 115·5[*] | 140·2 |

(To be continued).

ON THE

## ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 155).

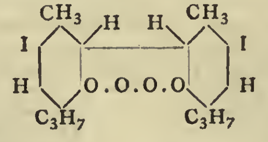
Another batch was prepared under the same conditions as those which yielded the red precipitate at 60° C., excepting that the fresh sample of caustic soda was used, as in the last case. The precipitate obtained was of a yellow-brown colour, similar in appearance to the large dilution one at the ordinary temperature, but of less sticky character. This was dried at a low temperature (40° C.), and when dry was of a yellowish white colour. It was then treated with boiling alcohol, and the alcoholic solutions filtered off. The united alcoholic solutions were then partially evaporated, when a considerable portion fell out of solution. The remaining solution was then filtered off, and the deposited portion collected, washed with alcohol, and dried. (Call this portion $\alpha$). The alcoholic solution which was filtered off was treated with a little water, when a flocculent yellowish white precipitate was obtained, which was filtered off, washed with water, and dried. (Call this portion $\beta$). The remainder of the original precipitate insoluble in alcohol was dissolved in ether, filtered, and recovered. (Call this portion $\gamma$).

*Analyses of* $\alpha$.

Total iodine:—
Quantity taken =0·1308 grm.
Silver iodide found=0·1062 ,, =43·86 p.c. iodine.

Combustion of same:—
Quantity taken =0·0957 grm.
Water found =0·0372 ,, = 4·31 p.c. hydrogen.
Carbon dioxide found =0·1460 ,, =41·60 ,, carbon.
By difference .. .. =10·23 ,, oxygen.

Those results may be fairly well represented by the formula $C_{20}H_{24}I_2O_4$, or constitutionally thus:—



Theoretical:—
C =41·23
H= 4·12
I =43·64
O =10·99

*Analyses of* $\beta$.

Total iodine:—
Quantity taken =0·1151 grm.
Silver iodide found=0·0902 ,, =42·34 p.c. iodine.

Combustion of same:—
Quantity taken =0·0830 grm.
Water found =0·0332 ,, = 4·44 p.c. hydrogen.
Carbon dioxide found =0·1259 ,, =41·36 ,, carbon.
By difference .. .. =11·86 ,, oxygen.

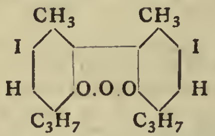
No likely single formula can be adduced from those results. They point to admixture of a compound of similar composition to the last one treated, together with one of similar constitution but containing less iodine, very probably one only of the benzene nuclei being substituted.

*Analyses of* $\gamma$.

Total iodine:—
Quantity taken =0·1824 grm.
Silver iodide found=0·1518 ,, =44·96 p.c. iodine.

Combustion of same:—
Quantity taken =0·0983 grm.
Water found =0·0376 ,, = 4·24 p.c. hydrogen.
Carbon dioxide found =0·1516 ,, =42·05 p.c. carbon.
By difference .. .. = 8·75 ,, oxygen.

Those results agree well with the formula $C_{20}H_{22}I_2O_3$, and may be constitutionally represented thus:—



Theoretical:—
C =42·55
H= 3·90
I =45·03
O = 8·51

A new batch of the excessive dilution product was prepared with the following proportions:—1·3 grms. thymol and 2 grms. caustic soda in about 5 litres of water (ordinary temperature). The precipitate, which was of a yellowish brown colour and would not settle as in the previous case, was filtered off, washed, and dried. The precipitate was then treated with successive portions of boiling alcohol, and the soluble portion of precipitate recovered. This was then treated with warm alcohol, in which a small portion was insoluble. The insoluble portion was filtered out and neglected. (It should be pointed out here that nearly all the compounds dealt with in this paper exhibit inter-solubility, that is, a solution of one will render to a slight extent soluble one which is otherwise insoluble in the solvent simple. The presence of iodine, free or "encluded," also seems to greatly influence the solubility. Probably the most important external factor capable of influencing the solubility is the presence of minute quantities of metal oxides of sufficiently intimate combination as to enable them to pass with the compounds into the lightest solvents. As was remarked at the outset, this fact has been taken advantage of throughout, and in some cases the fact may be further applied in order to effect separations by heating the mixture with a metal oxide and water, magnesia being a good one for the purpose).

The soluble portion was recovered from the alcohol, dissolved in ether, the ethereal solution floated on water in a stoppered vessel, and treated with sodium amalgam for three days. The product was then recovered, dried, and taken for analysis.

Total iodine of the partially reduced compound:—
Quantity taken =0·1094 grm.
Silver iodide found=0·0953 ,, =47·06 p.c. iodine.

Combustion of same:—
Quantity taken =0·0802 grm.
Water found =0·0292 ,, = 4·04 p.c. hydrogen.
Carbon dioxide found =0·1168 ,, =39·71 ,, carbon.
By difference .. .. = 9·19 ,, oxygen.
(The hydrogen was specially determined).

Those results may be represented by the formula $C_{36}H_{42}I_4O_6$.

The remainder of the partially reduced product was again dissolved in ether, transferred to a flask placed under an upright condenser, and treatment with hydrogen from zinc and sulphuric acid carried on for a week at a

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[*] This sudden fall of the atomic weight as observed in this fraction, which corresponded to an oxide lying between erbia and holmia, has been explained by further experiments, and will be discussed in a separate memoir in the *Zeit. fur Anorg. Chemie.*

slightly elevated temperature. At the end of this time a portion was taken for analysis.

Total iodine of the further reduced product :—
Quantity taken =0·0996 grm.
Silver iodide found=0·0834 „ =45·24 p.c. iodine.

Combustion of same :—
Quantity taken =0·1114 grm.
Water found =0·0494 „ = 4·94 p.c. hydrogen.
Carbon dioxide found =0·1854 „ =45·38 „ carbon.
By difference .. .. = 4·44 „ oxygen.

Those results show that the iodine and oxygen had now both been attacked, but, it will be observed, not proportionately. This will be important when the position of the iodine atoms come to be discussed.

The remainder of the further reduced product was transferred and treated in like manner with zinc-dust and solution of caustic potash for fourteen days more, the temperature being sufficiently raised to maintain the ethereal solution in a brisk state of ebullition. At the end of this time the product was recovered, when it was found to have parted with all its iodine. When dried it appeared colourless and transparent in thin layers, but amber-yellow in mass; it possessed a strong odour, somewhat pine-like, and was of soft and sticky consistence.

Combustion of the reduced product :—
Quantity taken =0·0836 grm.
Water found =0·0788 „ =10·47 p.c. hydrogen.
Carbon dioxide found =0·2744 „ =89·51 „ carbon.
(Only one analysis could be made).

It would thus appear to have been reduced to a hydrocarbon.

*Analyses of the Original Non-reduced Compound.*

Total iodine :—
Quantity taken =0·1021 grm.
Silver iodide found=0·0870 „ =46·03 p.c. iodine.

Combustion of same :—
Quantity taken =0·0796 grm.
Water found =0·0292 „ = 4·07 p.c. hydrogen.
Carbon dioxide found =0·1151 „ =39·43 „ carbon.
By difference .. .. =10·47 „ oxygen.

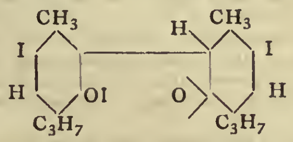
Formula, $C_{36}H_{42}I_4O_7$.

It is apparent that the effect of the first partial reduction was simply the removal of an atom of oxygen, which greatly strengthens the assumption as to the distribution of the oxygen atoms in the molecule, as pictured in the constitutional representation already given.

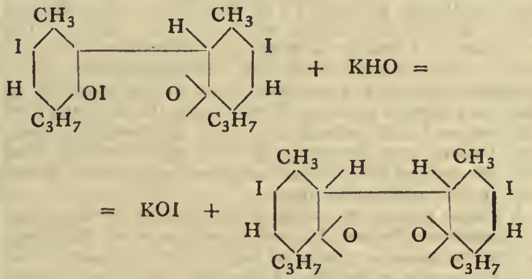
Messinger and Vortman in their paper treat of the action of iodine on thymol at considerable length. They were of opinion that the product of the reaction was a di-thymol iodide, but I consider that I have shown quite conclusively that no such compound is formed under any circumstances. As in the case of the phenols, they failed to recognise that they were dealing with a mixture of substances, and also the fact that the compounds contained iodine other than that of substitution. By boiling with a solution of potash and other means, they obtained a yellow body which they considered to be a decomposition product, which assumption was erroneous. The total iodine of this body they estimated as 47·24 per cent. On reduction they obtained a body which corresponded generally with Dianin's di-thymol, and they considered it to be, or to contain, a di-thymol molecule. The ultimate analysis, however, gave only 75·6 per cent carbon, whereas di-thymol requires 87·26 per cent. The results, they point out, agree better for an oxy-di-thymol, which requires 76·41 per cent of carbon.

The iodine percentage given above 47·24 agrees well with that given by me for a class of compounds which can be best represented by assuming the existence in the molecule of a ring of carbon atoms of the naphthalene type, and which could not possibly yield a di-thymol by reduction. Further, the percentage of carbon found by them for the reduced product could be much more easily reconciled by this assumption.

The red body they represent thus :—



and the formation from this of the yellow body, thus :—



(To be continued.)

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## NOTE ON EXPERIMENTS ON THE SPECIFIC GRAVITY OF GOLD CONTAINED IN GOLD-SILVER ALLOYS.*

By HENRY LOUIS, Singapore, Straits Settlements.

Four alloys of gold and silver were prepared, containing the metals in the following proportions by weight :—

1. Gold : Silver : : 1 : 2 62.
2. Gold : Silver : : 1 : 3·15.
3. Gold : Silver : : 1 : 4·11.
4. Gold : Silver : : 1 : 5·17.

These alloys were rolled, with repeated annealing, into thin strips, rather thinner than is usual for assay-cornets. The strips were thoroughly annealed, cut into pieces, and dropped into hot parting-acid. They were boiled with No. 1 parting-acid for one hour and ten minutes altogether, and then with No. 2 parting-acid for thirty minutes, washed thoroughly with boiling distilled water, and left under water under the exhausted receiver of an air-pump for thirty hours.

Their specific gravities were then taken with the following results, the temperature being 15° C. :—

| No. of Experiment. | Weight of Gold in Air. | Weight of Gold in Water. | Weight of equal bulk of Water. | Specific Gravity. |
|---|---|---|---|---|
| | Grains. | Grains. | Grains. | |
| 1. | 9·408 | 8·946 | 0·462 | 20·36 |
| 2. | 13·897 | 13 209 | 0·688 | 20·20 |
| 3. | 13·627 | 12·956 | 0·671 | 20·31 |
| 4. | 13·170 | 12·566 | 0·604 | 21·8 |

The quantities operated on were very small, and the balance and weights by no means first-rate, so that the results are not likely to be very accurate. The first three results are sufficiently close together, but the very high figure obtained in the fourth experiment must, in all likelihood, be due to some error. Hence, it will be safest

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* International Engineering Congress, August, 1893.

to average the results of the first three experiments, and, pending a more complete and accurate investigation, which I hope to make of this subject, to take the specific gravity of the gold residue left on dissolving the silver-gold alloys at about 20·3 at 15° C. Apparently the varying proportions of the two metals in the alloys do not affect the result.

Gold thus left, on dissolving out the silver, is highly spongy, and, on annealing, it undergoes a very evident shrinkage. The result now obtained proves that, on annealing, the molecule of gold does not contract, but, on the contrary, expands, the shortage of bulk being due to a diminution of the physical interspaces between the particles of gold, while the interatomic distances must increase, the diminution being, of course, greatly in excess of the increase.

With regard to the figures here given it may be noted that Rose obtained, for the sp. gr. of precipitated gold, results varying between 19·49 and 20·72. His figures, taken together with mine, seem to point clearly to the existence of a heavy allotropic modification of gold. It is, of course, possible that the brown amorphous gold obtained, either by precipitation or by the removal of the silver from a silver-gold alloy, may be a mixture of ordinary and allotropic heavy gold, in varying proportions: there can, however, be little doubt of the allotropism, and of the further fact that gold exists in the alloy in this allotropic form.

A further partial and indirect justification for this latter statement may be found in the experiments of Matthiessen on the specific gravity of alloys (*Phil. Trans.*, 1860, p. 177), in which he shows that the observed specific gravities of gold-silver alloys exceed the calculated ones (calculated upon the sp. gr. of ordinary gold) in the ratio, approximately, of 1 : 0·997. This would appear to suggest that the gold in these alloys is in a heavier state than ordinary normal gold; but any conclusions based on these observations are liable to modification, seeing that it is not yet known in what condition the silver in these same alloys exists.

It is possible that these results may afford a clue to the explanation of the widely different specific gravities found by different observers of native gold specimens (containing silver), of approximately the same composition, but from different localities.

In order to complete our knowledge of this subject it will be necessary to study the character of the gold by dissolving out the alloying metal from a series of alloys of gold with different metals, and I hope to be able to undertake this investigation before long.

The above experiments were conducted, by the kind permission of Prof. W. Chandler Roberts-Austen, in the research-laboratory of the metallurgical department of the Science Schools, South Kensington.

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# NOTES UPON THE COMPOSITION AND SOME PECULIARITIES OF MULES' MILK.

By A. B. AUBERT, M.S., and D. W. COLBY, B.S.

THE animal from which the milk was obtained is the property of Mr. McLaughlin, railroad contractor, and is now worked, singly or with mate, on the construction of the Bangor and Aroostook railroad; is about eleven years old; weighs 1100 lbs.; usual feed, hay and oats of good quality.

The mule showed no signs of heat previous to or at the time of milking; was milked several times a day, giving about two quarts of milk in all. Two samples of milk were received at an interval of about three weeks, the flow of milk having begun about six weeks previous to the sending of the first sample.

When received, the milk was of a pure white colour without yellowishness, of alkaline reaction, which upon being kept in a cool room it only lost on the eighth day, becoming slightly acid. In spite of this change in reaction no curdling as exhibited by cows' milk took place, but simply the separation of a very fine flocculent floating coagulum. The fat globules generally proved rather small, approximately ten per cent averaging 0·001 m.m. in diameter, forty per cent from 0·0018 to 0·0037 m.m.; forty per cent varied from 0·0037 to 0·0092 m.m., the remainder running from 0·0092 to 0·0222 m.m. and over.

A column of milk allowed to stand in a cool place for three days gave a separation of cream equal to one-seventeenth of the total height of the column. In the first sample of milk it was practically impossible to precipitate the casein with dilute acetic acid and carbonic anhydride.

By treating the milk with 70 per cent alcohol a white, fine, flocculent precipitate was obtained, which upon being filtered and washed with 70 per cent alcohol, strong alcohol, and lastly ether, dried and weighed, gave 2·52 per cent and 2·17 per cent of albumenoids, while by Kjeldahl's process 2·94 per cent of albumenoids were obtained, the factor used being 6·25.

The albumenoids of the second sample exhibited rather different properties from those of the first sample, precipitating more readily by the addition of dilute acid.

This milk was diluted with fifteen times its own volume of water, very dilute acetic acid added, carbonic anhydride was passed through for twenty-five minutes, and it was then set away in a cool place for forty-eight hours. A precipitate of casein was obtained, which proved most difficult to filter and wash. The results obtained were 2·33 per cent and 1·92 per cent, while the results by a method similar to Wanklyn's were 2·21 per cent and 2·42 per cent for total albumenoids. This would indicate that the quantity of albumen could not be greater than 0·5 per cent, if as much.

### RESULTS OF ANALYSIS.

*Sample No. 1 (Specific Gravity at 15°, 1·032).*

| | |
|---|---|
| Total solids .. .. .. | 10·65 per cent. |
| Fats .. .. .. .. .. | 1·86 „ |
| Albumenoids .. .. .. | 2·94 „ |

*Complete Analysis of Sample No. 2 (Specific Gravity at 15°, 1·033).*

| Analysis No. | I. | II. | III. | IV. |
|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Total solids .. | 10·92 | 10·86 | 10·81 | 10·83 |
| Albumenoids .. | 2·21 | 2·42 | — | — |
| Fats .. .. .. | 1·99 | 1·97 | 2·30 | 2·25 |
| Sugar.. .. .. | 6·07 | 5·96 | — | — |
| Ash .. .. .. | 0·52 | 0·53 | — | — |

I. and II. by A. B. Aubert; III. and IV. by D. W. Colby.

The fat in III. and IV. was extracted by petroleum benzene, which usually gives higher results than by ether extraction.

The only other American analysis of mules' milk which has come to our notice is that by E. F. Ladd (*Agricultural Science*, i., 108).

Below is given the composition of mules' milk, as well as that of the mare and ass. The similarity is very apparent.

| | Mules' milk. Average of analyses I. and II. | Mules' milk. Results of E. F. Ladd. | Average composition given in " Die Milch," by Hermann Scholl. | |
|---|---|---|---|---|
| | | | Asses' milk. | Mares' milk. |
| | Per cent. | Per cent. | Per cent. | Per cent. |
| Water.. .. | 89·14 | 91·59 | 89·64 | 91·00 |
| Albumenoids | 2·31 | 1·64 | 2·22 | 1·99 |
| Fat .. .. | 1·98 | 1·59 | 1·64 | 1·18 |
| Sugar .. .. | 6·04 | 4·80 | 5·99 | 5·31 |
| Ash .. .. | 0·53 | 0·38 | 0·51 | 0·43 |

Mares' milk, like that of the mule, is quite alkaline, remaining so for some time. It coagulates with difficulty, giving a very fine flocculent coagulum. The fat globules of asses' milk resemble those of mules' milk, being on the average very small.—*Journal of Analytical and Applied Chemistry*, vii., No. 6.

## ON CARBORUNDUM.

By WM. P. BLAKE.

A new abrasive material has been produced, and is in the market, for the various uses to which emery, or corundum, is applied. It is on exhibition in the metallurgical collection in the gallery of the Mines and Mining Building at Chicago by the Carborundum Company, of Chicago.

It is an artificial compound. The name which has been coined for it is misleading as to its composition, for it is not a compound of carbon and corundum, but is a definite compound, atom for atom, of carbon and silicon; a true silicide of carbon, or a carbide of silicon. The name carbo-silicon would have been more scientific and appropriate, but not as useful for trade purposes.

The appearance and properties of this substance are more nearly those of the diamond than of corundum, the lustre being highly vitreous and adamantine, and the hardness being extreme, sufficient, in the form of a rapidly rotating wheel, to cut the hardest steel and corundum crystals, and the material is said to have been used with success in polishing diamonds.

We owe the formation of this carbide of silicon to the prodigious chemical power of the electric current and the high temperature at which the carbon and silicon are brought together. The process and the apparatus are extremely simple. Carbon and silica are intimately mixed and are exposed to the force of the current in a simple trough or box made of firebrick or clay. The current flowing through the mixture reduces the silicic acid to metallic silicon, which unites with the carbon at one pole, while the oxygen passes to the other pole.

The crusts of the carbide so obtained are, on cooling, washed and cleansed in acid to remove soluble impurities, and are then crushed and sifted into different sizes to be used for making cutting-wheels, whetstones, or polishing-cloth. The cleansed crusts of carborundum are aggregates of very small but highly brilliant crystals, with highly polished faces, reflecting light like mirrors. The angles are sharp, and the general arrangement or grouping of the crystals is columnar, giving the masses a rude prismatic structure made up of tabular crystals.

The industrial and scientific world is indebted for the introduction and utilisation of this very important and interesting compound to Mr. Edward G. Acheson, of Chicago, who obtained a United States patent, and in June, 1891, organised a joint-stock company under the title of the Carborundum Company for its manufacture. In June, 1892, improvements in the process of manufacture had been made; the production was increased to 25 lbs. per day, and the price lowered to 2 dols. and 4 dols. per pound. In September, 1892, the manufacture of cutting and grinding wheels was commenced, and has since continued with increasing success. The present capacity of the works at Monongahela, Pa., for the production of the carborundum is said to be 100 to 150 lbs. a day. Its use at present is confined to the smaller-sized discs and wheels, which have found especial use and favour with the dental profession for cutting porcelain teeth and for other uses, for which they have hitherto relied on emery. It is claimed for the new wheels that they cut faster, are more enduring, and that they do not heat up the object being cut so much as wheels made of emery. An explanation of this may be found in the fact that the carborundum is an excellent and rapid conductor of heat, a decided advantage in many ways.

The physical properties of this substance, so far as I have been able to determine them, may be summarised as follows:—

*Crystallisation.*—Hexagonal. Generally in rhombic tabular plates, with angles of 120°, and the terminal edges of the prism bevelled, giving the following forms as seen, among others, in the field of a microscope, magnified about 20 diameters. The general habit is tabular, with long and irregular pedicles apparently shading off in a series of thin plates to the point of support or growth. Or, if viewed from the point of support or growth of the mass outward, the thickness and regularity of crystallisation increase by additional plates toward the end where the elongated irregular crystallisation ends in well-formed angles and brilliant planes, often showing in very fine parallel lines upon the edges, but without any foliation. The fracture is conchoidal and there is no evidence of cleavage. The edges are replaced by minute perfectly formed planes, and the intersection of these planes may give the appearance of striations when viewed by transmitted light in the microscope.

*Colour.*—As seen in mass by the reflected light, the dominant colour is bluish green, but varies from a pale yellowish green to dark blue green and emerald-green. Under the microscope, by transmitted light, the thin transparent plates have a pale green tint, but the depth of colour in the crystals varies, some being apparently nearly colourless or pale greenish yellow, while others are very dark olive-green, or emerald-green, much like the green colour shown by green tourmalines and by olivine. In some masses the colour and lustre are adamantine grey, a pale tint like that seen in rough uncut diamonds. A bronze-like lustre may also be seen on some samples with iridescence, reminding one of the tints of newly-formed crystals of bismuth. Fragments of a sapphire-blue colour have also been noted. When crystals are seen on edge, in a strong light, the colouring becomes more dense and pronounced. All the crystals appear to be perfectly transparent. When reduced to powder the colouring is lost, aud the fine powder is ash grey. As seen in the manufactured wheels the pervading colour is a light epidote green. I have not obtained any satisfactory evidence of dichroism, though this character is strongly suggested by the appearance of the compound. It has a high index of refraction.

*Specific Gravity.*—Nearly 3. One determination upon a small mass, freed from air by boiling, gave me 2·946.

*Hardness.*—The great hardness of carborundum has already been described, but carefully conducted tests are yet required to show its exact hardness compared with corundum and the diamond, and its exact comparative practical value as an abrasive substance compared with emery, corundum, and diamond powder. It will scratch sapphire, but not diamond, and its hardness is therefore between 9 and 10, or about 9½ on the hardness scale.

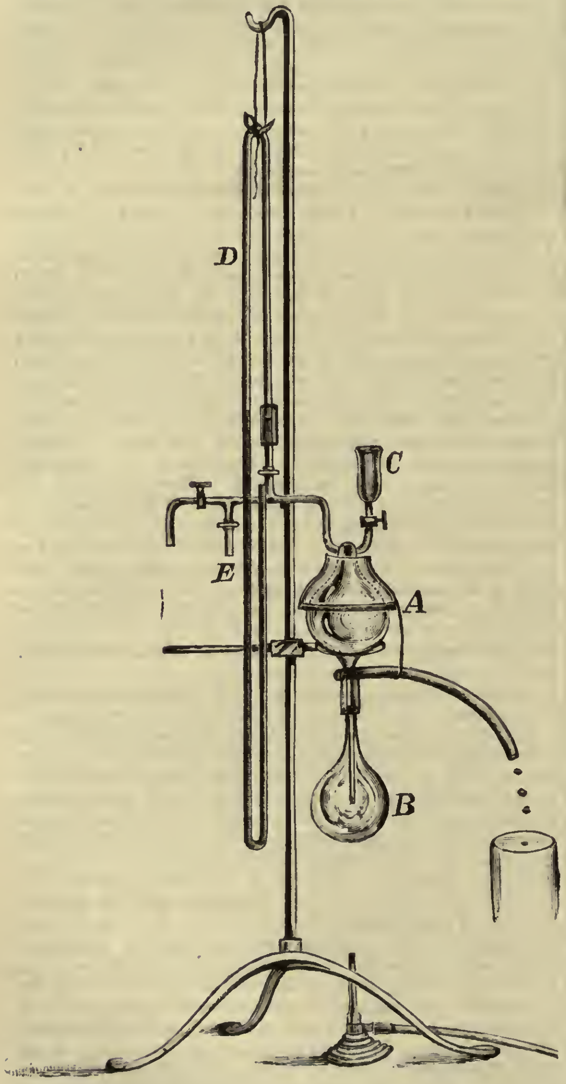
*Future Possibilities.*—This discovery and its application are of great industrial importance. While at present the quantity of the material produced daily is comparatively small, it would seem that practically there is no limitation of the amount of this substance which may be produced. The requisite conditions are cheap power, an abundance of clean sand and of carbon, and these are not difficult to find. We may expect at no distant day to see large grindstones made of it for ordinary purposes; its superior "grit" and cutting power making it much more desirable than the sandstone of which our grindstones are made. Or we may find it moulded into tyre-like rims to slip upon large core wheels for economy of material and speed of mounting, with maintenance of diameter.

If by any modification of the process, by possibly slower action, and an equable high temperature, long maintained, large crystals of this compound could be formed, we should have a brilliant gem added to our list of precious ornamental stones. Its fine colour, splendid adamantine lustre, and its hardness, all fit it to occupy a high place in the series of gems.—*Engineering and Mining Journal.*

## APPARATUS FOR EXTRACTION FOR ANALYSIS OF GASES DISSOLVED IN WATER.*

By EDGAR B. TRUMAN, M.D., F.C.S.,
Borough Analyst, Nottingham.

A GLASS flask, A, of 500 c.c. capacity, is joined by means of its tubular termination to a second lower flask, B, of 200 c.c. capacity, by means of a water-joint. In the lower flask is suspended from the upper one a thermometer, reading up to 150° C. From the neck of the upper flask proceed two millimetre tubes. The right-hand one, after receiving a stopcock, expands into a cup, C, having a capacity of 30 c.c. The tube on the left rises to the level of the bottom of the cup. This tube has two tubes supplied with stopcocks joined on to it at right angles—one above and one below. To the one above is attached, by a water or glycerin joint, a mercury tube, D, doubled on itself above and below, as shown, and having a length when so doubled of 880 m.m. This tube is graduated in m.m. from 0 to 400 in two directions, downwards in the open limb, and upwards in the long limb, starting in each case from the level of the horizontal tube. This tube is filled with mercury up to the zero points, and indicates the rate of exhaustion of the apparatus, and is also a test of leakage.



The second tube, a little further on, E, points downwards for attachment to a Geissler's water-pump. Still further on a stopcock is let into the main horizontal tube, which then bends downwards for communication with a Sprengel pump.

The apparatus is put into connection with both mercurial and water pumps, and the stopcock at the base of cup C is closed. By means of the water pump the apparatus is exhausted in a great measure of air; five minutes' pumping with a high pressure water produces a vacuum of 730 m.m., when the barometer stands at 753. The water-pump stopcock is then closed, and exhaustion is completed by the Sprengel in about thirty minutes more.

The liquid to be examined for gases is then, after measurement, introduced by the cup, C, into the upper flask, whence it flows into the lower one.

The liquid is allowed to stand for an hour, so that gases disengaged at ordinary temperatures may come off. These are collected by the Sprengel and analysed in the usual way.

The vacuum having been restored, heat is cautiously applied to the lower flask by means of a Bunsen burner. If carefully done there is no bumping. The effect of heat is, by disengaging gas, to increase tension, and to enable the water to become hotter. The mercury in the mercurial tube and that in the thermometer rises. When the mercury in both places remains constant the Bunsen burner is removed.

The gas given off by boiling is then collected and analysed.

## THE ACTION OF LIGHT UPON DYED COLOURS.*

(Concluded from p. 157.)

### CLASS IV.—FAST COLOURS. (WOOL). (*Continued*).

*Azo Colours.*

Wool Book I.
*Acid Reds.*—
87. Cloth red B. From amido-azo-toluene and α-naphthol-mono-sulphonic acid NW. S. and J. 115.
91. Orseillin BB. From amido-azo-toluene-mono sulphonic acid and α-naphthol-mono-sulphonic acid NW. S. and J. 124.
93. Cloth Red No. OB. From amido-azo-toluene and β-naphthol-di-sulphonic acid R. S. and J. 114.
97. Azo Fuchsin G. From sulphanilic acid and di-oxy-naphthalene (1·8)-α-mono-sulphonic acid. S. and J. 229.
98. Azo Fuchsin B. From toluidine and di-oxy-naphthaline (1·8)-α-mono-sulphonic acid. S. and J. 228.

Wool Book II.
*Chromotropes.*—
3. Chromotrope 6 B cryst.
4. Chromotrope 8 B cryst.
5. Chromotrope 10 B cryst.

*Induline Colours. Rosindulines.*

Wool Book I.
*Acid Reds.*—
95. Azo Carmine. Sodium salt of phenyl-rosinduline-di-sulphonic acid. S. and J. 369.

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* Read before the British Association (Section B), Nottingham Meeting, 1893.

* Report of Committee, consisting of Professor T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Nottingham Meeting, 1893.

### Class V. Very Fast Colours.

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

*Azo Colours.*

Wool Book II.

*Chromotropes.*—

1. Chromotrope 2 R cryst.
2. Chromotrope 2 B cryst.

*Oxyquinone Colours.*

5. Alizarin Red (alumina mordant).
10. Alizarin Turkey Red (cotton).

*Natural Colouring Matters.*

6. Madder Red (alumina mordant).
1. Cochineal Scarlet (tin mordant).
2. Kermes Scarlet (tin mordant).

### Silk Patterns.

The foregoing colours were dyed on silk, employing 2 per cent colouring matter, and the patterns were exposed to light, along with those on wool, with the result that the relative fastness of the various colours was practically the same as on wool.

### General Result.

The experiments extend at present over too limited a number of colouring matters to enable one to draw fixed general conclusions, but it may be well already at this point to record the following observations.

The most fugitive reds on wool and silk are the eosins and allied colours. Curiously enough, the introduction of the methoxy group, as in methyl-eosin, &c., increases the fastness, not of the colour as a whole, but of the pale faded tint which results after the first few weeks' exposure. As already stated, this tint remains practically unchanged even after a whole year's exposure.

With respect to the rosindulines, it is interesting to note that the G shades are very fugitive, while the B shades are moderately fast.

All basic reds belong to the more or less fugitive class, including, namely, the magentas, safranines, and rhodamines. The nature of the acid with which the colour base is combined seems to have no influence upon the fastness of the dyed colour.

Comparatively few (about twenty) of the azo reds examined are fugitive, and these belong chiefly to the simple monazo colours.

The great bulk of the fast and moderately fast reds belong to the azo colours, the so-called secondary diazo colours being generally faster than the rest. It is evident, however, that the fastness of these azo colours depends, not only on the base which is azotised, but also upon the character of the naphthol sulphonic acid employed. This is especially noticeable in the chromotropes, in which a particular dioxynaphthalene disulphonic acid is employed, and all of which are remarkable for their fastness. The particular azo compound and phenol united together is also of importance.

With respect to the milling and cloth reds, it does not appear that the use of mordants with them increases their fastness to light.

The number of very fast reds is extremely limited, but it includes both natural and artificial dyes—namely, madder, cochineal, kermes, alizarin, and the chromotropes 2 R and 2 B. When it becomes possible to expose the Congo reds, one or two others will no doubt have to be added to the list of very fast artificial red dyes. In this connection it may be pointed out that certain reds obtained from the natural dye-stuffs are fugitive, namely, those obtained from Lima-wood, Cam-wood, and the allied woods.

It is well to add that there are no sharp lines of division with respect to fastness to light among the various reds, and each of the five classes into which they have been here arbitrarily divided includes colours which differ from each other more or less in this respect.

# DETERMINATION OF THE TRUE ATOMIC WEIGHT OF COPPER.*

By Dr. GUSTAVUS HINRICHS, St. Louis, Mo.

Chemistry of precision is at present in a very peculiar condition, especially that branch thereof which has for its object the determination of the atomic weights of the chemical elements. On the surface it seems that this department is in a most flourishing condition; the number of determinations never was greater than at present, the space devoted to this topic in the chemical periodicals never was more extended, and the accuracy of the results is stated with an astonishing degree of precision, quite often expressed by means of refined methods of calculation, such as we formerly used to meet in astronomy only.

Under such conditions it is exceedingly unpleasant to be in duty bound to present an abundance of facts which demonstrate that all this glory is but a hollow mockery and a sham, and it even becomes difficult to obtain a hearing for the purpose of submitting these facts for examination. Since the very renown of Stas depends upon the failure of chemists to practise mathematical and chemical criticism, it can scarcely be expected that these faculties will now respond promptly to our call after having been dormant for a quarter of a century. Our modern chemist seems to be as unwilling to find errors in the work of Stas as philosophers were to look through the first telescope for spots on the sun.

Nevertheless the recorded facts show that the eminent analyst of Brussels has entangled the entire subject of the atomic weights in a web of systematic errors both chemical and mathematical, and has besides committed some of the most astonishing errors in the detail of his work.

However unwilling chemists may be to look doubtingly at the work of their recognised master, it seems worth trying to make them join us in the critical examination of the work of a disciple of the school of Stas. To bring it more nearly home to the chemical public of this day and of this country, let us select for such examination the work of recognised merit recently completed by an American chemist according to the general methods of Stas, with the single exception of the use of enormous quantities, which much-extolled peculiarity of Stas was one of the worst features of his system.

In looking over the entire field, I can find no example more fair for this critical examination than the work of Professor Theodore W. Richards on the atomic weight of copper. This work has been republished in full in Germany, in the new *Zeitschrift fur Anorganische Chemie*, Bd. I., 1892. The results thereof have been accepted as practically final by Ostwald (*Zeitschrift*, ix., p. 383, 1892), who is generally recognised as an authority on the subject of atomic weights. I will further add that I have the highest regard for the analytical skill of Prof. Richards, who has spent on this work four years of his time in the best appointed laboratory of research in America.

If therefore I am constrained to declare that the final results of Prof. Richards are without permanent value to chemistry, being nearly one-fifth of 1 per cent in error; that, moreover, this entire research was superfluous, because a more accurate determination was known before this work was published; and that finally the only two reliable results which he obtained in his laborious research were not recognised by him as such, but were with great labour and much chemical acuteness blotted out from his

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* See accompanying letter

work by himself; if I shall be compelled to declare all of this, I shall equally insist that the fault thereof is not in the excellent chemist personally, but is due to the school, the system of Stas which he represents.

To keep this paper within reasonable bounds, it will be necessary to proceed directly to the determination of the atomic weight of copper; thereafter the critical part can be very briefly given.

The electrolytic ratio 2Ag : Cu is 3·402, if we adopt temporarily 63·5 as the atomic weight of copper, and take Ag at 108 as standard. For 63 and 64 the ratio would be 3·375 and 3·438.

Now the determinations of Shaw (1886) gave 3·400; Lord Rayleigh found 3·404 to 3·408, and Gray 3·401. These values are almost identical with the one corresponding to 63·5 as the atomic weight of copper. This therefore *is* approximately the value sought. It only remains to find the minute deviation of this number from the true atomic weight, or to establish that this deviation is zero.

The mean value given by Richards himself is Cu 63·61, resulting from the means of all his eleven series, oxygen being taken as 16·000. Of course this mean involves the use of several of the erroneous values of Stas; but as in the different series the elements employed are different, it is impossible to make allowance for these errors in the general mean. Part of the variation of the individual means is due to this fact; they run from 63·593 to 63·641. The actual range of these means is 0·048, or say 0·05.

Professor Richards next throws out six of his eleven series, and thereby reduces the range to 0·008, or say 0·01 in the means of the series retained, and gets 63·604 as a sort of selected final mean. This is a tacit admission that more than half of his series were made according to methods not fit to yield results of precision. This final selection of the best agreeing results is quite generally practised in the school of Stas to-day. Thus Van der Plaats freely omits entire series of Stas, according to his own sweet will and pleasure (*Annales de Chemie*, vii., p. 512, 1886). The most glaring example of the kind—a genuine parody on sound science—may be found in Van Laar's "Thermodynamics" just published (p. 8). Having tabulated the results obtained by the different chemists—and he seems to consider the determinations of Leduc and Lord Rayleigh as legitimate determinations of atomic weights—he says drily, and with absolute unconcern, "If we except the value under *a* as being certainly too low, and those under *d* and *e*, which are certainly too high, we get, as mean of the values under *b* and *c*, 15·881—exactly the value of Morley. For O = 16, then follows H = 1·0075." This work is highly commended in a Preface by van 't Hoff, and has been equally highly recommended by Oswald. The selection made by Richards, therefore, is in keeping with the practice of the school, for which it would be unjust to blame the individual.

Next the question arises, Is the value 63·61, or say 63·60, of Richards, the true atomic weight of copper? In that case the deviation of 63·5 would be 0·10. But the determinations of Richards showed a range of 0·05, which is exactly half of the quantity in question. No scientist will pretend that a quantity is established with precision when it is affected with an uncertainty of half its own value. In other words, the work of Richards has *not* established the atomic weight of copper at 63·6.

A careful examination of the methods used by Richards in his eleven series compels the condemnation of ten thereof as unfit for the purposes of precision. Only the use of *blue vitriol* as material, and the electrolysis and dissociation thereof, remain as legitimate processes for the determination of atomic weights. Of such determinations Richards has made three excellent series. The results obtained, expressed in parts by weight in hundred thousand, are as follows, the reference page being to the German edition:—

| Series | I. | II. | III. |
|---|---|---|---|
| Page | 162 | 168 | 171 |
| Copper | 25455 | 25450 | 25448 |
| Water | 35958 | 36067 | 36067 |
| At degrees C. | 250 | 360 | 370 |

Professor Richards also determines the amount of sulphuric acid left after electrolysis; it is the ghost of Stas demanding the famous *complete analyses* at the expense of precision. Richards uses a *volumetric* process for this purpose, involving two indicators, also pure sodium carbonate, hence demanding the exact value of the atomic weights of sodium and of carbon. Such complex processes will give concordant results in so skilful hands as those of Richards; but the unknown residual errors make the final result useless in chemistry of precision.

Now right here Prof. Richards loses himself in the labyrinth of Stas. Summing up the three ingredients determined, Richards finds a deficiency of *five* in *ten thousand* outstanding. In other words, 1 m.grm. of blue vitriol in every 2 grms. has been lost—a quantity entirely too large to be overlooked in chemistry of precision.

Not knowing that volumetric processes can claim no place in the determination of the precise value of atomic weights, Prof. Richards thinks his sulphuric acid determination right; he is properly certain of his copper determination; hence he concludes that the error can only have occurred in his determination of the water of crystallisation. He now pushes the heating of the blue vitriol to the dissociation of the sulphate. He reaches a dark red heat. He thus has secured that elasticity which Stas utilised in the precipitation of the silver chloride, and which Richards alone has properly condemned in his work on the atomic weight of barium.

However, Professor Richards is too good a chemist to hide for himself the very unsatisfactory outcome of this search for the missing substance. He admits the absence of the necessary *evidence*, but says: "There is no doubt of its great probability." This is one of the classical phrases of the school of Stas. It has absolutely no place in the chemistry of precision.

Professor Richards adds:—"Upon such a matter it is difficult to see how more definite results could have been obtained." He does not know that he had the most definite and admirably exact results when he started out on this chase after the lost water, not dreaming that it was the acid that had been lost by him. He thus throws away the only valuable determinations of his four years of work. But, also, this stupendous error is due to the school he follows.

To show this in the shortest manner possible, let us adopt the atomic weights of H = 1 and S = 32, established by my limit method, and also put Cu = 63·5; the analysis thereafter will show how much the "deviation" of this atomic weight amounts to. Thus the formula—

$$CuO_4S + 5H_2O$$

for the atomic weights specified requires per hundred thousand parts of blue vitriol—

| | |
|---|---|
| Copper | 25451 |
| Water | 36072 |

It is plain that these calculated values are practically identical with those found by Professor Richards given in the preceding pages. The correction to be applied to the observed values to obtain the calculated values are—per hundred thousand parts of blue vitriol—as follows:—

| Series | I. | II. | III. |
|---|---|---|---|
| Copper | −4 | +1 | +3 |
| Water at 360° | | +5 | +5 |

The agreement is remarkable; the error of the determinations is only *one milligrm. in twenty-five grms.* if we take 4 as the mean of the above numbers. Thereby these determinations of Richards stand in the front rank of atomic weight determinations. That he failed to see this and started upon the long chase for more water is exclusively due to the dense fog that for a quarter of a century has been darkening this entire field of chemistry, so that at present, not only the old, but also the young, chemists seem to have lost the faculty of sight in the broad light of day, and refuse to look at truth.

Thus it is established by these two determinations of Richards—the only two accurate ones in his entire research, but which he himself, as faithful Stasian chemist, had corrected away from truth—enable us to assert that the deviation of the true and exact atomic weight of copper from 63·5 is certainly not over 0·002.

A series of determinations carried on in accordance with the conditions of my limit method will no doubt show that *the atomic weight of copper is exactly* 63·5 in the mathematical sense.

In conclusion, I beg leave to express the hope that the young chemists—at any rate, those in this country—will no longer take part in the blind worship of an authority that has covered the immortal work of Dumas and Berzelius with the rubbish of a spurious accuracy and an imaginary analysis, and hereafter rather assist in the determination of the true and exact values of the atomic weights of the chemical elements.

*To the Editor of the Chemical News.*

Your journal has contained very brief and misleading notices of my recent papers on atomic weights. I do not wonder at this; the subject being quite intricate, thanks to the indirect combinations made use of by Stas and his admirers.

I have therefore thought it desirable to take up a single case, and have selected that of copper, which Stas did not meddle with. The determinations of Richards (whose papers you have reprinted) are generally accepted as the best. I have carefully examined them, and offer you the result for the Chemical News in the paper enclosed.—G. H.

**Announcement.**—We are requested to mention that Mr. W. Brown, of 11, Dale Street, Liverpool, is now assisted by Mr. George Stevens, who until lately practised in Liverpool on his own account as an analytical chemist. Mr. Stevens is considered one of the most expert sugar chemists in Great Britain.

**The Use of Calcium Plumbate in the Analysis of Ashes.**—K. Wedemeyer (*Archiv der Pharmacie*).—The formation of calcium plumbate from calcium carbonate and lead oxide is not as expeditious as Kassner alleges. The experiments took a favourable course in as far as the combustion of the organic matter was very rapid.

**Valuation of Hides for Glue.**—F. Gantter.—The author takes an average portion of the sample in question (100 grms.), adds to it 1 litre of water in an evaporating basin, adds a few drops of soda-lye, and boils until the hide is entirely dissolved. The liquid is made up exactly to 2 litres in a suitable graduated vessel, and allowed to subside for ten hours. Of the clarified solution 20 c.c. (=1000 grms. of substance) are evaporated to dryness, dried at 105°, the residue is weighed, and its ash is determined. He thus finds the crude glue-ash. A second portion, of 10 c.c., is placed in a graduated flask holding 100 c.c., diluted with 30 c.c., neutralised with acetic acid, and solution of tannin is added as long as a precipitate is formed. The flask is then shaken up and filled to the mark. This solution, which contains the non-precipitable constituents "not glue" along with the slight excess of tannin, is filtered through a dry folded filter, a sufficient quantity of hide powder to precipitate the tannin, and the mixture is allowed to stand for ten hours. If after this time the solution gives no further tannin reaction, it is filtered, and the dry matter (free from ash) in 50 c.c. of it (=0·500 grm. of substance) is determined. If this is multiplied by 2, and deducted from the ascertained weight of crude lime (free from ash), the remainder is the quantity of pure lime.—*Zeitschr. f. Anal. Chem.*, xxxii., Part 4.

## CORRESPONDENCE.

### ARRANGEMENT OF CHEMICAL LECTURES.

*To the Editor of the Chemical News.*

Sir,—A recent paper by Professor Lothar Meyer in the *Berichte der Deutsch. Chem. Gesell.*, xxvi., 1230, has now been abstracted in the September number of the *Transactions of the Chemical Society*, p. 408. It treats of Prof. Meyer's system of arranging his lectures in accordance with the periodic arrangement of the elements, instead of adopting the traditional plan of arbitrarily dividing elements into ill-defined groups of metals and non-metals, a plan sanctioned by antiquity, but hardly defensible on any other ground.

I take this opportunity of strongly urging on those of your readers who are engaged in teaching chemistry to give this plan a trial. I have used it with great success since 1884, and have published two text-books of which this system forms the basis. Prof. Meyer is perfectly correct in his statement that this method of treatment saves a great deal of time; but other inducements towards its adoption might be readily suggested. It ensures the consideration (if desired), in its correct place, of each and every discovered compound; it renders the facts of chemistry, which by their number and apparent arbitrariness tend so frequently to dishearten students, easily remembered; and it teaches the use of that all-important guide in all chemical work, analogy.

Prof. Meyer differs, however, from the method I adopt in certain details. I consider it on the whole advisable to consider methane along with hydrogen chloride, water, and ammonia; and I do not think it desirable to treat of *all* the compounds of hydrogen with other elements before taking up the more simple halides. But such minor changes may well be left to individual taste.

It is, however, in my opinion, very important that the student should realise that chemistry is not a cut-and-dry store of facts, but is in active progress; and it appears to me proper to draw attention, where possible, to gaps in our knowledge. Students worth their salt invariably conceive a desire to complete such series of compounds, and often offer suggestions which, whether practicable or not, always lead to some profitable talk.—I am, &c.,

William Ramsay.

University College, London, W.C.
September 30, 1893.

**Rapid Dialysis of Liquids.**—C. E. Linebarger.—The author's device is especially distinguished by its automatic supply of water. It consists of a funnel suspended by means of wire to one end of the beam of a balance; into the funnel is introduced the filter of parchment paper, receiving the liquid to be dialysed and previously well soaked in water.—*Zeitschrift fur Analyt. Chemie*, xxxii., Part 3.

**Arrangement for Determining the Quantity of a Volatile Ingredient present in any Substance.**—O. Petterson (*Chemiker Zeitung*).—The apparatus consists of two vessels of equal size in juxtaposition, each of which is connected with one limb of a differential manometer. By means of cocks the vessels can be shut off from the manometer or connected with the air. In the manometer there is a displaceable thread of liquid. If into one vessel there is introduced a liquid containing a known quantity of a known volatile substance, and into the other one containing an unknown quantity of the same to be ascertained, and both vessels after being placed in communication with the manometer and then with the air are then exposed to a given equal temperature, the position of the liquid thread in the manometer shows in which vessel is the substance with the smaller proportion of volatile constituents.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 12, September 18, 1893.

**Periodic Maxima of Spectra.**—M. Aymonnet.—This paper is drawn up in such a manner that it does not admit of useful abstraction, whilst it is not of sufficient importance to claim insertion in full.

*Revue Universelle des Mines et de la Metallurgie.* Vol. xxiii., No. 2.

**Volumetric Determination of Copper, Iron, Antimony, and Zinc-powder.**—The methods proposed are those of F. Jean and Weil, and they have been already noticed under the *Bulletin de la Soc. Chimique de Paris* and the *Zeitschrift fur Analyt. Chemie.*

*Zeitschrift fur Analytische Chemie.* Vol. xxxii., Part 3.

**Analysis of Tobacco and its Preparations.**—Dr. Viktor Vedrödi.—This paper is too voluminous for insertion in the Chemical News.

**On Sjögvist's Method for the Determination of Free Hydrochloric Acid in the Gastric Juice.**—Stan. Bondzynski.—The author concludes that the Sjögvist process is the most trustworthy method of determining the physiologically effective hydrochloric acid.

**Cadmium Mirror Obtained from Zinc-powder on the Examination of Urine for Mercury.**—According to E. Ludwig's method, mercury is precipitated from urine by means of zinc-powder. It is necessary to remark that commercial zinc-powder contains cadmium. Zinc-powder, according to Ludwig's method, was somewhat strongly heated in a covered porcelain crucible. When cold it was placed in a tube stoppered with asbestos, superstratified with copper, and the open end of the tube drawn out to a point and closed by fusion. On moderate heating, not exceeding the temperature necessary for the expulsion of the mercury, a metallic mirror was obtained which in appearance could scarcely be distinguished from a mercurial mirror. On stronger ignition, shining globules were observed at the beginning of the capillary part of the tube closely resembling drops of mercury, but on the touch they proved to be hard granules of metallic cadmium. The proportion of cadmium in the zinc-powder used was 1·63 per cent. It was not completely removed by strong ignition, as cadmium is volatilised very slowly. The same zinc-powder, after ignition for an hour in a current of hydrogen, still retained 1 per cent of cadmium. An examination of the metallic mirror obtained by the iodine test must never be omitted. Or copper-powder or copper-turnings may be used instead of zinc-powder.

**A New Method for the Detection of Cotton-oil in Lard and Olive-oil, and on an Approximate Estimation of Cotton-oil in Lard.**—F. Gantter.—Cotton-oil now occurs in commerce which does not show Becchi's reaction—blackening in contact with silver nitrate. The author therefore proceeds as follows:—He places in a test-glass 1 c.c. melted fat or oil (which must be clear as water), dissolves it in 10 c.c. of petroleum ether, allows a drop of concentrated sulphuric acid to fall into the solution, and shakes it up briskly at once. The colour phenomena thus produced are very distinct, and show characteristic differences in the behaviour of various fats. Pure lard if thus treated takes a colour from a pale straw to a faint reddish yellow. The solution remains at first clear, but there are by degrees separated heavy drops of a strong reddish yellow colour, whilst the supernatant liquid remains of a scarcely yellowish colour, in most cases clear as water. Cotton-oil, on the contrary, takes at once a deep brown or black colour, and retains this colour on very prolonged standing. Mixtures of lard and cotton-oil take a more or less deep brown according to the proportion of the latter. The dark colour appears if only 1 per cent of cotton-oil is present in lard. Olive-oil on similar treatment behaves quite similarly to lard. Earth-nut oil behaves like cotton-oil. A pure lard must give with the sulphuric acid test merely a straw-yellow or at most a reddish yellow. The iodine number must not exceed 27.

**The Use of the Fluoresceine Reaction for the Detection of Saccharin in Beer.**—F. Gantter.—Already inserted.

**Separation of Barium, Strontium, and Calcium.**—R. Fresenius.—Already inserted.

**The Ascent of Saline Solutions in Filter-paper.**—E. Fischer and E. Schmidmer (*Liebig's Annalen*).—Already inserted.

**The Change in the Specific Gravity of Nitric Acid in Consequence of the Presence of Hyponitric Acid.**—G. Lunge and L. Marchlewski (*Zeit. f. Angew. Chem.*).—The authors show that great errors may be committed by depending solely on the specific gravity of acids. They give a table showing alteration in the specific gravity by the presence of $N_2O_4$ in quantities varying from 0·25 to 12·75 per cent.

**A Volumenometer.**—A. v. Kalecsinsky.—This apparatus is quite similar to that described by A. Paalzow.

**Instruments for Determining High Temperatures in Flues, &c.**—F. Fischer (*Zeit. fur Angew. Chemie*).—This paper requires the four accompanying cuts.

**Examination of the Behaviour of Fuel in Watery Vapour, Air, and Carbonic Acid.**—F. Fischer.—This paper requires the accompanying figure.

**Air Pyrometer.**—This instrument was described in its original form in *Zeit. Anal. Chemie*, xxix., 62, and has been remodelled by J. Wiborgh (*Stahl and Eisen*, xi., 913).

**A Modified Cornu Photometer for High Temperatures.**—Le Chatelier (*Comptes Rendus*, cxiv., 214 and 340).

**A Critique of Le Chatelier.**—H. Becquerel (*Comptes Rendus*, cxiv., 255 and 390).

**Le Chatelier's Thermo-element for the Measurement of High Temperatures.**—Emilio Damour.—Already inserted.

**Convenient and Uniform Division of Samples of Ores.**—H. L. Bridgman.—From the *Journal of Analytical and Applied Chemistry.*

**Instrument for Sampling Liquids.**—O. Steinba.—It consists of a tube open below, with a sheath open laterally, and enclosing the lower end elastically, in which the tube can slide up and down.

**Arrangement for Washing Precipitates.**—Matthew Forbes.—From the Chemical News.

# NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Water Freezing in Pipes.**—Can any of your correspondents kindly tell me how I can make the water in hot water pipes non-freezing? We warm our works with hot water, low pressure. Last winter, one Sunday night, it froze and burst the pipes. I suppose it will do so this winter, unless we go on Sunday and fire the boiler.—A. P. Jevon.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1768.

## REMARKS ON THE CHEMISTRY OF BACTERIA.*

By R. WARINGTON.

The immense variety of substances produced in the vegetable kingdom has always been a source of astonishment to the chemist. The plant is, indeed, the finest chemical laboratory with which we are acquainted. While some kinds of chemical work are common to all plants, there is hardly a species which does not possess some special capacities—which does not produce some products different from its neighbours. When we survey the whole vegetable kingdom, the extent to which this specialisation is carried, and the immense variety of the products obtained become simply overwhelming. Chemists are still unacquainted with the larger part of the substances produced by plants. When we turn from the products of plant work to the materials employed our wonder still increases, for these materials are of the simplest kind—water, carbonic acid gas, oxygen, nitric acid, and a few inorganic salts—yet out of these the whole of the immense variety of vegetable products is constructed.

This being the case, we need hardly say that the *methods* of plant chemistry are of supreme interest, both to the chemist and to the vegetable physiologist. By the aid of what forces, through what course of reactions, are the simple materials moulded to their final issue? The higher plants are in some respects unfavourable subjects for the study of plant chemistry. Their different parts have different functions, and the changes in progress are obscured to the student by the fact that changes of a very different type are in progress at the same time, and in places very near to each other. What would not the physiologist give if he could isolate a single cell, and grow it by itself in solutions of known composition; when by studying the nature of the cell's new growth, and the variations taking place in the nourishing solution, he might hope to be able to grasp the facts of cell nutrition, and the nature of its waste products? Such an opportunity is actually afforded when we study the chemical changes brought about by bacteria.

In bacteria we have the vegetable cell in its simplest form: we have a mass of protoplasm and a cell-wall, but the cell is single or united with a few others, and, as far as we know, the life changes in all the cells of every species living under the same conditions are the same. Moreover, these organisms grow freely in suitable solutions, and the chemical changes produced in the materials held in these solutions can be readily ascertained. We have thus in a study of the chemistry of bacteria a splendid opportunity for enlarging our knowledge of plant chemistry, and, indeed, of becoming acquainted with the fundamental reactions on which synthetical organic chemistry depends.

The study of the chemical work performed by bacteria has occupied as yet but a few years, but the results have been most remarkable. The immensely numerous species of bacteria have been found to exhibit an almost equally great diversity of action. Different members of the class have been found to flourish under entirely opposite conditions, to feed on wholly different materials, to perform an immense variety of chemical work upon the media in which they live, and yet the chief product of plant life—the formation of protoplasm and cell-wall—is probably in each case practically the same. The study of the chemistry of bacteria has thus greatly enlarged our conceptions of the chemical power of the vegetable cell.

As a contribution to the discussion to-day, I propose to call attention to the chemical actions displayed by three species of bacteria existing in the soil, and all of first-class importance in their relations to agriculture.

It is well known that all ordinary soils contain organisms possessing a vigorous power of oxidising—of bringing about a combination between the oxygen of the air and various organic and inorganic bodies. Thus dead vegetable and animal tissues in soil are, under favourable conditions of heat and moisture, resolved into carbonic acid, water, and nitric acid.

Particular experiments show that the nitrogen of albumin, gelatin, asparagine, urea, ammonia, ethylamine, and thiocyanates is converted by soil into nitric acid. Nor is the action confined to organic matter; for nitrites are oxidised to nitrates, iodides to hypoiodites and iodates, and bromides to hypobromites and bromates.

The organisms producing nitric acid have been made the subject of study by many chemists, and after much labour and many disappointments they have been satisfactorily isolated.

We now know that the production of nitrates in the soil—a process of the greatest importance for the nutrition of agricultural crops—is accomplished by the action of two organisms, each of which performs a distinct stage in the work. By one organism ammonium carbonate is oxidised and the nitrogen converted into a nitrite. By the second organism nitrites are converted into nitrates. We have here an excellent example of the way in which certain special functions, certain narrowly limited lines of work, are exercised by individual species of bacteria. The nitrous organism can oxidise ammonia to nitrite, but it cannot change a nitrite into a nitrate. The nitric organism, on the other hand, oxidises nitrites readily, but it cannot oxidise ammonia. Both organisms are present in all fertile soils, but the formation of nitrites is not usually perceived, as they are at once converted into nitrates.

The organisms we have mentioned grow and exercise their functions in dilute solutions of appropriate composition, and it is therefore possible to study exactly the mode of their nutrition.

Like every other living organism, they develope and perform their functions only when certain inorganic salts supplying phosphates, sulphates, potassium, calcium, and magnesium are present. The continued omission of one of these has been proved in several cases to bring about a cessation both of growth and function. The general fact is familiar to physiologists, but it is singular that we have as yet no rational idea of the mode in which these various inorganic bodies assist in plant nutrition, with the exception of the fact that sulphur, and possibly in some cases phosphorus, are constituents of albuminoid bodies.

As to nitrogenous food, these organisms are amply furnished by the ammonia, the nitrite, or nitrate which is intentionally added to the solution; the addition of no other nitrogenous substance is necessary. Here, too, we are on familiar ground. Ammonia and nitrates are both well known as the most appropriate nitrogenous food for plants.

When we inquire, however, what is the source of carbon to the nitrifying organisms, we are confronted by a startling novelty. It is found to be quite unnecessary to supply these organisms with any carbonaceous food save carbonates, bicarbonates being preferred. The fact of the conversion of carbonates into organic cell substance has been conclusively proved in the case of the nitrous organism; it is at present assumed to be also true of the nitric organism, as this also requires the addition of no organic carbon to its nutritive solution.

The fact that green plants exposed to sunlight are

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* A Paper read before the British Association (Conference of Sections B and D), Nottingham Meeting, 1893.

capable of forming organic substances from the carbonic acid and water of the atmosphere is well known to physiologists, but it is equally certain that this action does not occur in the dark. Yet here we have a colourless cell, destitute of chlorophyll, growing in the dark, which, nevertheless, is capable of decomposing carbonic acid, and producing from it carbonaceous cell-substance. From a purely chemical point of view this reaction may well appear at first sight incredible, as the decomposition of carbonic acid is an action requiring the consumption of much energy, which in the case of the green plant is supplied by the sun's rays, but in the case of the nitrifying organism is supplied in no such way.

This theoretical difficulty disappears, however, when we look at the whole reaction brought about by the nitrous organism. This organism attacks carbonic acid in its combination as ammonium carbonate, and the formation of an organic carbon compound proceeds at the same time as the oxidation of the ammonia; the result of the whole reaction being the liberation of heat, and not its consumption. A supply of external energy is thus not required.

Expressed in its simplest terms, the green plant manufactures carbohydrates from carbonic acid and water by a consumption of solar energy as follows:—

$$CO_2+H_2O=CH_2O+O_2.$$

The nitrous bacterium oxidises ammonium carbonate, producing at the same time ammonium nitrite and a carbohydrate: this reaction we may express in its simplest form as follows:—

$$(NH_4)_2CO_3+O=NH_4NO_2+CH_2O+H_2O.$$

The equation, however, by no means fully expresses what actually occurs, as Winogradsky finds that 35 parts of nitrogen as ammonia are oxidised for one part of carbon assimilated; the whole reaction is thus strongly exothermic.

The nitric organism multiplies more slowly than the nitrous, and does not therefore afford so good a subject for quantitative experiments; its nutrition has not yet been fully studied.

The last organism I wish to speak of is the one of which Winogradsky has given a preliminary description during the present summer. It has been obtained from soil, and possesses the remarkable power of assimilating the free nitrogen of the atmosphere. To accomplish this assimilation it is simply necessary to grow it in a solution containing sugar (dextrose) and the necessary salts, no combined nitrogen being supplied. Under these circumstances a vigorous growth of the bacillus takes place, the sugar undergoes a butyric fermentation, and at the end of the operation it is found that the culture has acquired nitrogen, the amount being apparently about $\frac{1}{500}$th of the weight of the sugar fermented. By using as much as 7 grms. of sugar, an assimilation of 14 m.grms. of nitrogen has been obtained. Washed air, free from ammonia and nitrates, was used in these experiments.

That a vegetable organism should be able to acquire from the air the whole of the nitrogen which it needs is certainly very remarkable, and is an extraordinary fact both to the physiologist and chemist.

We have no clue as yet to the mode in which the nitrogen enters into combination; but it is evident that in this case, as in the nutrition of the nitrous organism, the difficult piece of chemical work forms but a small part of a much larger reaction that is at the same time in progress, and with which it is essentially connected.

It seems not improbable that these results of Winogradsky will explain some facts which have hitherto presented much difficulty. That a special organism, when in union with the roots of a leguminous plant, is capable of bringing about the assimilation of the free nitrogen of the air is now admitted by all; but it is denied by Schlœsing and other accurate observers that the same organism when living in the soil has any such property. May we not suppose that for the assimilation of nitrogen to occur the organism must be supplied with sugar or its equivalent, and that this supply of sugar to the organism only takes place when the organism gains access to the sap of one of the higher plants.

In conclusion, I think we shall all agree that, however imperfect is our knowledge of the chemistry of the three species of bacteria we have considered, the facts which have been established have at least enlarged our conception of the capabilities of a vegetable cell, and I trust that some light has also been thrown on the general method by which some of the extraordinary chemical results are attained.

## ON A NOTTINGHAM SANDSTONE CONTAINING BARIUM SULPHATE AS A CEMENTING MATERIAL.*

By Professor FRANK CLOWES, D.Sc.

The author draws attention to papers presented by him to former meetings of the British Association ("British Association Reports," 1885, p. 1038, and 1889, p. 594). These papers described sandstone extending over a large area at Bramcote and Stapleford, in the immediate neighbourhood of Nottingham, in which crystallised barium sulphate occurred in large quantity. Bramcote and Stapleford Hills and the Hemlock stone were wholly composed of such stone. The largest quantity found in the specimens analysed reached 50 per cent; complete analyses were given of specimens of sandstone from different parts of this district. The sulphate was in a beautifully micro-crystalline condition, and the crystals had been identified and separated both by Professor Lebour and by Mr. J. J. H. Teall. In some parts of the sandstone the barium sulphate uniformly permeated the mass. In other parts the sulphate occurred in streaks or network, the latter distribution leading to a curious mammillated weathering of the surface of the rock, owing to removal of the uncemented grains. Occasionally the cementing material occurred in nodular patches, as seen in sections of the sandstone; this led to the formation of the so-called "pebble sand-beds" at the top of one of these sandstone hills. The beds were the effect of weathering; the uncemented sand-grains became loose sand, and disseminated amongst the loose sand were the "pebbles," consisting of masses of sand-grains bound together by barium sulphate. The author has not been able to obtain from any source evidence of the occurrence of similar sandstone in any other part of this country; he is still without direct evidence whether the sulphate has been deposited as such, as in the colliery boxes of Durham, or is the result of chemical change occurring between calcium sulphate in solution coming into contact with barium carbonate already deposited in the sandstone.

## ON ERBIA.†

By GERHARD KRÜSS.

(Continued from p. 166).

According to the points of view now established there were then united as—

*Erbia Material No.* 5,

*Series* 9, fractions 2, 3, 4, and 5; and
*Series* 8, fractions 3, 4, and 5.

These earths were again dissolved as chlorides, fractionated by precipitation with aniline, and yielded—

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* Read before the British Association (Section B), Nottingham Meeting, 1893.

† *Zeitschrift fur Anorganische Chemie.*

*Series* 10.

Weaker bases ←—. —→ Stronger bases.

| 1 | 2 (very slight) | 3 (heavy precip.) | 4 (small residue) |
|---|---|---|---|
| 172·4 | 172·9 | 162·7 | — |

The fractions 1 and 2 of this series were doubtless nearly pure ytterbia (Yb=172—173), and after the examination of the values found on determining the equivalents of fractions 2 and 3, the separation of erbia from ytterbia seemed to have been effected much more easily than in former series of decompositions, where the erbia-material was still of a complicated composition.

Fraction 4 of Series 10 was intentionally selected small in order, as far as possible, to keep back all erbia (which now especially contained all the earths of low equivalents, Ho=161, Tr=157, Yb=90) in the third fraction of Series 10. This fraction 3 with $\overset{\text{III}}{R}=162·7$ therefore forms—

*Erbia Material No.* 6.

From this point the erbia material was no longer fractionated by heating the nitrates or, as latterly, by simple precipitation with aniline, but it was alternately resolved into aniline precipitates and aniline solutions by the action of aniline hydrochlorate. In this manner the most feebly basic and the most strongly basic portions were separated, so that finally there was left a "mean" portion. This has proved to be the most effective method for working up earths supposed to be almost pure. As regards details, I refer to my earlier treatise on this subject (*Zeitschr. Anorg. Chemie*, iii., 108—115).

The erbia material No. 6 yielded on this fractionation—

*Series* 11.

Feebler bases ←—.
Precipitates.

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| 167·9 | 167·9 | 169·6 | 167·8 |

—→ Stronger bases.
Solutions.

| Mean. | 4 | 3 | 2 | 1 |
|---|---|---|---|---|
| 168·6 | 161·5 | — | 158·3 | — |

If we bear in mind that this erbia material was fraction 3 of Series 10, and if we compare the values which have been found for fractions 1 and 2 of Series 10 with those of the first and second precipitates of Series 11, we see that in Series 10 by a fortunate manœuvre the erbia has been at once abruptly separated from ytterbia. Further, the analysis of the four precipitates, as also of the middle Series 11 gave values approximately corresponding with the atomic weight of erbium. Here, therefore, exactly the same phenomenon was observed as that previously encountered by P. Cleve and others, *i.e.*, on isolating the reddish earth from a mixture of yttria earths, the atomic weight of $\overset{\text{III}}{R}$, calculated from the determinations of the equivalents of the earths, approached more and more to the number 166, or to a rather higher value, remaining almost constant on further fractionation. At the same time the solutions of these earths showed sharply the lines in the absorption spectrum marked Erα, Erβ. All these facts taken together might readily lead to the conjecture that in the reddish yttria earth (erbia) there is present an unitary oxide, and that this erbia earth contains a trivalent element of the atomic weight 166, 167, and 168. The following experiments caused this assumption to appear unwarranted.

In order to obtain the erbia earth containing probably $\overset{\text{III}}{R}=166$ to 168 from the "aniline solutions" of Series 11, there were united—

Solution 4+3+2 of Series 11.

From this mixture the more strongly basic portion was eliminated by two successive solutions; the residue of the material was used as the "middle" of Series 11, and the neighbouring precipitates, 4 and 3 (Series 11), were added. Thus after the elimination of the stronger bases, this entire middle part of the erbium material of Series 11 was united in order to be subsequently submitted to purification by treatment with aniline hydrochlorate.

There were taken—

Weaker bases ←—. "Aniline precipitate," —→ Stronger bases. "Aniline solution."

| | 1 | Middle | 1 |
|---|---|---|---|
| Series 12. | — | 166·6 | — |

and this precipitate (No. 1, Series 12) to which, according to the entire course of the transaction, there corresponded a value of more than 166·6 (= middle of Series 12) is added to the precipitates 1 (167·9) and 2 (167·9), Series 11. These three fractions, with values between 167 and 168, formed—

*Erbia Material No.* 7.

This, when decomposed with aniline hydrochlorate, gave—

Weaker bases ←—. Aniline precipitate. —→ Stronger bases. Aniline solution.

| | 1 | Middle | 1 |
|---|---|---|---|
| Series 13. | 167·4 | 167·0 | — |

The aniline solution 1 (Series 13) stands towards the side of stronger basicity, and must join to the middle of Series 12, for in obtaining the erbium material No. 7 only the aniline precipitate 1 of Series 12 was used.

There were therefore mixed:—Solution Series 13 and middle Series 12, and from this mixture the most feebly basic part was separated out by precipitation with aniline. For the $\overset{\text{III}}{R}$ of this earth there was found the value 167·8; according to the entire system of the experiments, this was to be united with the precipitate and with the middle of Series 13. Thus was obtained—

*Erbium Material No.* 8.

This consisted, therefore, of the portions $\overset{\text{III}}{R}=167·4$, 167·0, 167·8. Since the feebler bases (ytterbia earth) had been well removed from the erbia material No. 5 by Series 10, and since in the erbia material No. 6 the stronger bases had been more and more separated by the solutions of Series 11, the true erbia earth had united in the erbia material No. 8 as a reddish oxide, with the Er spectrum lines and the values 167·4, 167·0, 167·8 for Er. In the operations carried out with erbium material No. 6 and 7, especial care had been taken to remove the more strongly basic parts from the erbia. After these portions finally consisted of oxides with $\overset{\text{III}}{R}$ of 166·6, the erbia No. 8 now remaining must consist almost exclusively of an unitary earth if an $Er_2O_3$ exists. Hence the attempt was made to furnish the proof of the homogeneity of material No. 8, in the first place by fractionation, in order then to undertake exact determinations of the atomic weight of erbium.

This erbia earth was now treated by partially dissolving the hydroxide in aniline hydrochlorate. Thus, by directly succeeding aniline solutions, there were obtained fractions 1 to 3, and the precipitate remaining from the third fraction was called fraction 4. The erbia was thus resolved into—

Stronger bases ←—. —→ Weaker bases.

| | 1 | 2 | 3 | 5 |
|---|---|---|---|---|
| Series 14. | 164·0 | 165·8 | 168·7 | 170·3 |

The above experiments show that if erbia earth is still mixed with other erbia earths (ytterbia and yttria), in fractionating the earths we seem gradually to come nearer the isolation of an unitary earth, exactly as if there existed an erbium with an atomic weight between 165 and 168. When the weaker and stronger basic portions are removed, the properties of the erbia earth are no longer affected by those of other earths, and it no longer appears so stable, and behaves with aniline hydrochlorate like a non-unitary oxide—like a mixture or a compound of oxides of different equivalents.

This subject will be more minutely explained below.

(To be continued.)

## A SIMPLE METHOD OF STERILISING WATER FOR DOMESTIC PURPOSES.

By FRANCIS WATT,S F.I.C.,
Analyst to the Government of the Leeward Islands.

Some time age it became necessary to devise a process for the removal of suspended finely-divided particles of clay from water, for a delicate technical process. Considerable difficulty was experienced in rendering the water quite bright; some of the finer particles of clay remaining suspended rendered the water opalescent, and such forms of filter as could be used failed to remove this opalescence. It occurred to me to experiment with various precipitates which could be produced in the water and carry down with them these troublesome particles. Finally, the formation of aluminium hydrate was decided upon, and this was accomplished by adding alum, or some other suitable aluminium salt, in small quantities to the water and precipitating with lime water. The precipitate was allowed to subside and the water drawn off. The most troublesome waters were found to be rendered quite bright by this treatment.

Subsequently, the problem of purifying considerable quantities of water for drinking purposes was presented to me, when it appeared reasonable to suppose that if the fine particles of clay were removed by the aluminium hydrate, other minute bodies, and amongst them any micro-organisms that happened to be present, would be largely removed also. But in this case the use of ferric hydrate suggested itself, on account of the readiness with which it parts with its oxygen to organic matter, it being thought that some additional purifying effect would be derived from this.

Experiments were undertaken to ascertain the effect upon the micro-organisms of precipitating ferric hydrate in the water in question. The water being a moderately hard one merely required the addition of a small quantity of a nearly saturated solution of ferric chloride for a precipitate to form; this was filtered through sterilised filter paper, and small quantities of the water introduced into nutrient solutions. In practically every case, no development of micro-organisms took place even when the solutions were kept for over a week. Similar tubes were treated with the water before the addition of the iron solution, and growth in every case followed in eighteen hours.

These experiments have been repeated at intervals over a period of two years, and always with the same results. Even when small quantities water are drawn from the mass in which the ferric hydrate has subsided, without filtration, the supernatant water appears to be sterile.

It would appear, then, that we have here a simple process for rendering water for drinking and domestic purposes sterile with but little trouble or loss of time, and that this process will render water as completely sterile as boiling will. Boiling water for drinking purposes is always a troublesome operation; the quantity to be operated upon is usually greater than can be dealt with conveniently; a considerable time elapses before it is fit for use, and, when ready, the flat mawkish taste is objectionable; in fact the operation is rarely faithfully carried out, save in time of panic.

To carry out the process suggested in the case of a hard water, it suffices to add sufficient solution of ferric chloride (which should be as nearly neutral as possible) to produce a perceptible precipitate, the carbonates dissolved in the water being in many cases sufficient to effect this. In the case of a soft water—*i. e.*, one in which no precipitate is produced on the addition of ferric chloride, after the ferric chloride is added—a small quantity of lime-water, or of dilute solution of carbonate of soda, is thrown in, and this causes a precipitate to form. It is found that vigorous stirring promotes the granulation and subsidence of the precipitate.

The precipitate is allowed to subside, and the clear water is drawn off for use. It is often preferable to pass the water through some simple form of filter, such as a felt bag, or through clean sand placed in a shallow box, or in a flower-pot, in order to keep back any particles of the precipitate which may have been disturbed in the operation of drawing the water; but with large quantities of water this is seldom necessary.

It is found that 1 to 1½ fluid ounces of strong solution of perchloride of iron (British Pharmacopœia strength) are sufficient to purify 100 gallons of water. For domestic use it is advisable to dilute the solution considerably, say 10 times, and to use a teaspoonful of the diluted solution for each gallon of water.

If a sufficient quantity of water for one day's use be treated at night, a supply of pure water will then be ready for use every morning, with a very moderate expenditure of trouble or money.

With prevalence of diseases capable of being spread by the use of polluted drinking water, it would seem worth while to make a trial of a process which appears at once efficient, inexpensive, and equally applicable to large or small quantities of water.

A memorandum of this process was published in the *Official Gazette of the Leeward Islands*, xviii., No. 48, Nov. 27, 1890, since which time the process has been employed in public institutions and private houses in this Colony, with apparently good results. It would at least be interesting if others repeated these experiments with a view to their correction or confirmation.

## GELATINOUS SILVER CYANIDE.*

By LEE K. FRANKEL.

In the *Comptes Rendus* (lxxiii, 998) Stas has described the occurrence of four different varieties of silver chloride, viz.—

(*a*) The gelatinous.
(*b*) The cheesy, flocculent.
(*c*) The pulverulent.
(*d*) The granular crystalline variety.

No methods are given for obtaining these varieties, nor could the author find any reference in the literature to any other salts of silver having the above properties. The following will therefore be of interest.

Recently the author instructed one of the students in the University laboratory to reduce silver chloride to metallic silver by fusion with potassium cyanide. As the work was purely experimental, no weighed quantities of the substances were taken, nor was any notice taken of the temperature at which the fusion took place. The cooled mass and porcelain crucible were placed in a beaker, covered with water, boiled for thirty minutes, and then put aside until the following day. On examining the contents of the beaker, instead of finding the liquid above the crucible clear, as had been expected, it was filled with a transparent gelatinous mass, somewhat resembling aluminum hydrate, but of greater consistency. A portion of this precipitate was removed from the solution, carefully washed with cold water until the filtrate reacted neither with silver nitrate nor with dilute hydrochloric acid, and then carefully dried.

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* Read before the Chemical Section of the Franklin Institute, June 20th, 1893.

A qualitative examination showed the following:—The substance is readily soluble in ammonium hydroxide, from which solution it is re-precipitated by nitric acid. It does not fuse on heating, but decomposes readily, leaving a residue of metallic silver. The presence of cyanogen was readily detected by the "prussian blue" reaction. No chlorine was found.

A quantitative estimation of the silver in the substance gave a result which was 5 per cent lower than the theoretical amount of silver in silver cyanide.

This is in all probability due to the impurities contained in the compound, which arise from the potassium cyanide used in its preparation.

The amount of substance used in the analysis was very small, since what appeared to be a rather large quantity of the original, moist, gelatinous compound, shrivelled to a very small bulk on drying.

Repeated attempts have since been made to procure more of the substance for analysis, but all efforts have so far been futile. The amounts of silver chloride and potassium cyanide used have been varied, and the fusion likewise has been made at different temperatures, but without success. It is the intention of the author to fuse silver cyanide with potassium cyanide, and thereby to obtain the desired result.

## ON CARBORUNDUM.

By E. G. ACHESON,
President of the Carborundum Company.

The author read a description of carborundum at the meeting of the Franklin Institute, June 21st, and recites his early experiments, as far back as the year 1890, for the production of crystallised carbon in the electric furnace, which led to the formation of the carbide of silicon, to which he gave the name carborundum, under the supposition that he had formed a combination of carbon and aluminium, the mixture in the furnace originally consisting of carbon and corundum, for which, later, a mixture of carbon, silex, and common salt was substituted. Salt was found to be beneficial in facilitating the fusion and in protecting the mass from oxidation. Experience has shown that a good proportion for the mixture is 20 parts of carbon, 25 parts of sand, and 10 parts of salt, by weight. A core of carbon is used to connect the poles, and is found unaltered after the operation, it being surrounded by the mixture, while it serves to conduct the current, and by its resistance to transform the electrical energy into heat energy. In later forms of the furnace four carbon electrodes are used at each end of a rectangular box, or trough, built of fire-brick, and 6 ft. long, 18 in. wide, and 12 in. deep. The core is tabular and extends nearly the length of the box. An alternating, and not a direct, current is used. To produce 150 lbs. per day of twenty-four hours requires an expenditure of 78 h.-p. for a like period, amounting to 12 h.-p hours for each pound of carborundum produced. A furnace of the capacity and construction named requires from seven and a half to eight hours' time to complete the transformation of a portion of the charge into 50 lbs. of carborundum, and three charges are worked in twenty-four hours.

The carborundum as removed from the furnace is a mass of crystals incrusting the core in comparatively loose radial aggregates, which are crushed in water, and then digested with dilute sulphuric acid for seven days, to remove iron and other impurities. It is found that the crystals are not acted upon by any of the acids, not even hydrofluoric acid, which may be used to remove any excess of silica, nor are they affected by a current of hot oxygen by which any excess of carbon is removed, but they are slightly acted on by the caustic alkalis and the carbonates of the alkalis, and are decomposed by fusion with carbonate of soda. Analysis of a sample well cleaned by the above indicated methods showed the composition to be:—Silicon, 69·10; carbon, 30·20; with small quantities of alumina, iron, and lime as impurities, the presence of which gives the colour, for if pure carbon and pure silicon are used the crystals are white.

The author gives the results of several analyses by Dr. Mulhaeuser, the company's chemist. He found the specific gravity of some of the green crystals to be 3·22. Prof. J. W. Richards found the specific gravity as 3·123 for the green crystals, and that the blue crystals have a lower specific gravity.

A crystallographic examination has been made by Prof. B. W. Frazier, of Lehigh University, who finds that the crystals are rhombohedral, their disc shape being due to the predominance of the basal pinacoid. He says:—"The observed forms consisted of numerous direct and inverse rhombohedra with the basal pinacoid, and in some crystals the prism of the first order. In some crystals the rhombohedral symmetry was evident, in others the direct and inverse rhombohedra of the same parameters were found on the same crystal, so as to impart to it an appearance of holohedral hexagonal symmetry. This holohedral habit was observed in bluish green and blue crystals, while in those yellowish green crystals which were examined in the goniometer the habit was rhombohedral.

The value for the length of the vertical axis, calculated from four good measurements, was found to be C = 1·2264. An examination in polarised light gave the interference figure of an uniaxial mineral, thus confirming the determination of hexagonal symmetry made by measurements with the goniometer. The author also directs attention to the fact that W. P. Schützenberger, in May, 1892, in a communication to the Academy of Sciences of France, described the manufacture of a new chemical compound of simple formula, the symbol being SiC. This was three months after Mr. Nikola Tesla had exhibited an electric lamp containing carborundum (silicide of carbon), the composition of which was not, however, known at that time.

The author states that the powder of carborundum has been successfully used in polishing diamonds, and he believes that in the form of a very fine powder it compares favourably in hardness and cutting qualities with diamond powder of equal fineness.—*Engineering and Mining Journal.*

## CONSPECTUS OF THE MOST USUAL METHODS FOR SEPARATING THE OXIDES OF THE CERIUM AND YTTRIUM GROUPS.

By Professor GERHARD KRÜSS.

### I. *Drawn up Crystallising-out Double Salts.*

A. Potassium double sulphates used by Berzelius for separating the gadolinite and cerite earths. The substances precipitated are:—Scandium, terbium, cerium, lanthanum, didymium (Mosander, *Journ. Pr. Chemie*, 1843), dysprosium (Delafontaine), samarium (Bettendorf, *Liebig's Annalen*, 263), but also erbium (Nilson, *Ber. Deutsch. Chem. Ges.*, 1882; Krüss, *Liebig's Annalen*, 263).

*a.* As a modification, double sodium sulphates for the separation of philippium and terbium on the one hand (Delafontaine, (*Compt. Rend.*, 87), and of yttrium and cerium on the other (Erk, Naumann, *Jahrb.*, 1870).

B. Double ammonium nitrates for separating La and Di (according to Auer von Welsbach, *Monathshefte f. Chemie*, 1885); also for separating La and Di according to Schottländer (*Ber. Deutsch. Chem. Ges.*, 1892). Cerium is also precipitated, if present, as $CeO_2$.

*a.* Double sodium nitrate was used by Auer von Welsbach for resolving didymium into praseodymium and neodymium.

C. Potassium double oxalate, used by Delafontaine and

Mosander for separating Er, Y, and Di, as the latter also forms an insoluble double salt (Krüss and Bröckemann, *Lieb. Ann.*, 265).

### II. *Separation by Precipitation of Basic Salts.*

This method is naturally available for all earths which separate out in the order of their basicity.

A. Fuming off the nitrates, Berlin's method, elaborated by Bahr and Bunsen. Thus Marignac obtained Tr; Nilson Yb and Sc (*Ber. Deutsch. Chem. Ges.*, 1879, 1880); Clève, pure Er (*Compt. Rend.*, 91; Clève, as also Damour and Deville, separate in this manner Ce, La, and Di. According to Krüss and Nilson (*Lieb. Ann.* 265; *Ber. Deutsch. Chem. Gesell.*, 1887, 1888) this method is inadequate.

Here must also be mentioned the method of Frerichs, who mixes the solution of La and Di with such a quantity of sulphuric acid that on exaporating down only a part of the nitrate is converted into sulphate. On gentle heating only the nitrates are converted into insoluble basic compounds (*Ber. Deutsch. Chem. Ges.*, 1874).

B. Mixture of the solution of nitrates with oxides of the same material, when basic nitrates are deposited on heating. Scholtländer proceeds in the same manner for separating La and Di (*Ber. Deutsch. Chem. Ges.*, 1892). Hermann had previously used a similar method for separating La and Di, as had also Erk and Clève.

Here must be included the method of Frerichs, who separates La and Di by passing chlorine over the oxide. There are formed didymium chloride and lanthanum oxychloride, which in an aqueous solution are transformed into didymium oxide and lanthanum chloride.

C. Decomposition with excess of water. In this manner basic cerium salts are separated (Bunsen and Vogler, *Journ. Pr. Chem.*, 1858).

### III. *Separation by Fractionated Precipitation of the Earths in various other Forms of Combination.*

A. With ammonia, according to Mosander and Delafontaine. Clève (*Comp. Rend.*, 97) employed this method for purifying Sm, as also for separating La and Di (*Bull. Soc. Chim.*, 21). Crookes endeavoured, in like manner, to resolve yttria into five or eight constituents (Chemical News, liv.). Lecoq de Boisbaudran arrived partially in this manner at the discovery of his dysposium in Clève's holmium (*Comptes Rendns*, 1886); compare also Krüss (*Lieb. Ann.*, 265).

B. With aniline in alcoholic solution (Krüss, *Lieb. Ann.*, 265).

C. With oxalic acid, according to Mosander and Delafontaine. Bunsen and Zschiesche separate La and Di in this manner.

D. Formic acid, according to Delafontaine and Marignac, for obtaining terbia; also for obtaining philippium according to Delafontaine (*Comptes Rendus*, 87).

E. With excess of ammonium carbonate. According to Marignac and Krüss, Di alone is precipitated in this manner (*Lieb. Ann.*, 265).

### IV. *Separation by Partial Solubility.*

A. In water. La and Di as sulphates are placed in ice-water, and the solution heated to about 40°. Lanthanum sulphate separates out. Mosander, Holzmann, Krüss, and Bröckelmann (*Lieb. Ann.*, 265).

B. In alcohol. In the preparation of pure didymium nitrates (Bröckelmann, *Lieb. Ann.*, 265). For separating decipium and didymium sulphates (Delafontaine).

C. In acids. Mosander and Delafontaine employ for separation the partial solubility of the oxalates in nitric acid. Holzmann separates in this manner La and Di (*Liebig and Kopf. Jahrb.*, 1862); the former as oxalate is more readily soluble in nitric acid. Marignac proceeds similarly (*Ann. Chim. Physique*, [3], 27).

### V. *Separation by Oxidation.*

Cerium alone comes here into consideration.

A. In the dry way. On igniting the nitrates of the cerite earths CeO is oxidised to $CeO_2$; La and Di remain unchanged, and dissolve in dilute nitric acid (Mosander). Debray (*Comptes Rendus*, 1883) melts the nitrates of the cerite earths with potash saltpetre, whereby CeO is oxidised. Bunsen (*Ann. Chem. Pharm.*, 105) ignites the oxides with magnesium oxide. $ThCeO_2$ thus formed is dissolved in concentrated nitric acid; the solution is poured into dilute nitric acid, when cerium dioxide is thrown down. This method, however, was abandoned by Bunsen himself. Auer von Welsbach converts CeO into $CeO_2$, and allows it then to crystallise out as ammonium double nitrate (*Monatsh.*, 1884). Schöttlander proceeds in a similar manner (*Berichte*, 1882).

B. In the moist way. By introducing chlorine into the solution of earthy salts mixed with alkali in excess, Cer alone is precipitated as $CeO_2$. The other hydroxides pass into solution as chlorides. Mosander (*Journ. Pr. Chem.*, xxx., 1843) arrived in this manner at the discovery of lanthanum. By passing Cl into the solution of the chlorides mixed with sodium acetate, or by boiling the solution of the neutral chlorides (mixed with sodium acetate) with sodium hypochlorite, $CeO_2$ is formed (Popp, *Ann. Chem. Pharm.*, 131). Winkler separates Ce, La, Di, by mixing the solution of chlorides with mercuric oxide, and adding permanganate until a red colour is obtained. Ce and Di are precipitated (*Journ. Pr. Chem.*, 1865). Stolba proceeds in like manner (*Bohm. Ges. d. Wissensch.*, 1878). According to Gibbs, the cerite earths are precipitated as nitrates with $PbO_2$; according to Zschiesche, they are heated as sulphates with $Pb_3O_4$ and nitric acid, when $CaO_2$ is thrown down.

If we look over the above large number of methods of separating we see that, in proportion to the number of earths to be separated, an unusual number of appliances is available. Nevertheless, we cannot yet separate even two of these earths quantitatively from each other without combination or a very frequent repetition of the single methods. This behaviour greatly impedes the examination of these bodies, especially when we have to decide whether an earth is single or compound. Perhaps the results of the following experiments will be of some use in this direction.

Finally, it is my agreeable duty to thank Dr. Karl Hofmann for his admirable assistance in carrying out the above experiments.—*Zeitschrift fur Anorganische Chemie.*

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 165).

Among the lines enumerated various impurities may be represented, as I have indicated, at the passages in question. But this affects the here exclusively interesting fact relative to the profusion of rays in the region concerned in a vanishing degree only.

The appended numbers refer to the labels of the plates.

All the proofs were executed without a condenser, with a slit width of 0·040 mm. and of very sensitive plates (Zettnow's). The time of exposure varied, and is given specially for each spectrum.

*Cadmium*, No. 2039.—Exposure, six minutes. Twenty-two new lines, two of them beyond 185·2; the most effective (4) in the immediate neighbourhood of the same length, mostly pale and moderately sharp.

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

*Antimony*, No. 2040.—Exposure, five minutes. Twenty-eight new lines, three of them beyond 185·2; the most effective (3) near wave-length 182·9. Except the three most refrangible all are distinctly shown, several very intense.

*Bismuth*, No. 2043.—Exposure, six minutes. Twenty new lines, three beyond 185·2; the most effective at $\frac{1}{3}$ (Nos. 31 to 32). Most of them, especially the three most refrangible, pale and moderately distinct.

*Cobalt*, No. 2044.—Exposure, six minutes. Eighty-three new lines, twelve beyond 185·2; the most effective (9) near No. 31 towards No. 30. A large part of the lines intense and sharp; the remainder, including all beyond 185·2, very pale.

*Platinum*, No. 2045.—Exposure, six minutes. Eighty-one new lines, fourteen beyond 185·2: the most effective (15) nearly uniformly distributed over the spectrum, and surpassing in sharpness all the above-named spectra.

*Copper*, No. 2046.—Exposure, six minutes. Six new lines, one beyond 185·2; the most effective (2) near No. 30. All, even the palest, sharply drawn.

*Lead*, No. 2047.—Exposure, seven minutes. Six new lines, one beyond 185·2; the most effective close to the second component of No. 31; all the others very pale and indistinct.

*Iron*, No. 2048.—Exposure, ten minutes. Seventy-two new lines, four of them beyond 185·2; the most effective (4) between Nos. 31 and 32, but nearer to the former. The four most refrangible scarcely perceptible, the remainder more intense, but the less intense among them also imperfectly defined.

*Calcium*, No. 2049.—Exposure, seven minutes. Seven new lines, four of them beyond 185·2. Of the three most effective one coincides with the more strongly deflected component of No. 31, whilst the two others form the extremity of the entire spectrum. The less refracted of these two exceeds in efficiency all the lines situate beyond 185·2 of all the spectra here in question.

*Arsenic*, No. 2065.—Arrangement of experiment as in the foregoing proofs. Exposure, probably eight minutes. Twenty new lines, six beyond 185. Except these six all strong, but not clearly defined.

*Sodium*, No. 2103.—Exposure, twenty minutes. A single new line, scarcely deviating perceptibly from the second component of No. 31, moderately clear, but slightly intense.

*Silver*, No. 2107.—Exposure, three minutes. Twenty-eight new lines, six beyond 185·2. All the lines, except a single one situate near No. 31, and on its more refrangible side, very pale and chiefly indistinct.

*Gold*, on the same plate (No. 2107).—Exposure, seven minutes. Twelve new lines, three beyond 185·2. Of the five most efficient, three lie near No. 30, and a strong double line lies near No. 31, in both cases on the more refrangible side; all the others are very indistinct, even more so than with silver.

*Nickel*, No. 2108.—Exposure, seven and a half minutes. Twenty-six new lines, seven beyond 185·2; of the three most efficient two are near No. 30 and one a little less refrangible than No. 32. The entire region very pale, but well defined.

*Tin*, No. 2111.—Exposure, ten minutes. Eighteen new lines, three beyond 185·2. Except a single line, which lies in the middle between Nos. 31 and 32 and developes an enormous energy, all the lines seem melting away and are pale and very indistinct.

*Potassium*, No. 2112.—Exposure, five minutes. A single line, of faultless design and great intensity, coinciding exactly with the more refrangible component of No. 31.

*Tungsten*, No. 2113.—Exposure, ten minutes. Seventy-five new lines, twenty-one beyond 185·2; all nearly uniformly distributed, but forming distinct groups with single well-marked lines. The intensity of this band, so rich in lines, decreases uniformly towards its more refrangible end. The design of the lines is uniformly clear.

*Silicon*, No. 2114.—Exposure, ten minutes. Eleven new lines, five beyond 185·2; one only intense and sharp, coinciding exactly with the more refrangible component of No. 31.

*Chromium*, No. 2132.—Exposure, seven minutes. Eleven new lines; only traces beyond 185·2, one only well-marked and coinciding with the more refrangible component of No. 31. All the rest very pale, and most of them perceptible only with difficulty.

*Thallium*, No. 2133.—Exposure, eight minutes. Eight new lines, three beyond 185·2; the four most efficient form a striking group between Nos. 31 and 32, the components of which decrease in intensity and mutual distance with the wave-length. Here again a line coincides with the repeatedly mentioned component of No. 31; but it is very pale, scarcely more than a trace. The design of the entire proof is very clear, even in the more refrangible lines.

*Molybdenum*, No. 2136.—Exposure, eight minutes. Forty new lines, four beyond 185·2; the six most efficient are between Nos. 30 and 31, all very pale, the most refrangible mere traces, design of all being clear.

*Mercury*, No. 2139.—Exposure, seven mintes. Twenty-six new lines, nine beyond 185·2; the most efficient of all is close before No. 31; two other lines, likewise very energetic, are close to Nos. 30 and 32. The lines beyond 185·2 are associated as a group of lines, rapidly increasing in intensity, and gradually decreases with the growth of their natural distance. The sharpness of the lines is moderate.

*Magnesium*, No. 2143.—Exposure, seven minutes (width and slit exceptionally only 0·030 m.m). Three new lines are only distinct, coinciding with the more refrangible component of No. 31. Nothing visible beyond 185·2.

*Zinc*, No. 2144.—Exposure, thirty-two minutes. Seventeen new lines, one beyond 185·2. One of the two most efficient lines again coincides with the more refrangible component of No. 31; the other, more strongly deflected, lies closely to the same component. The entire region appeared very pale.

(To be continued.)

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ON THE

# ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 167).

## ARISTOL.

The article of modern materia medica known as aristol is taken by some to be a di-iodo-dithymol, by others a dithymol di-iodide, the latter being that now generally received. Aristol formed the subject of an abstracted note (*Pharm. Journ.*, May 2, 1891), in which free iodine was mentioned as an impurity. Pure aristol, according to Herr Reuter (*Apoth. Zeit.*, Jan. 28, p. 61), dissolves in ether with a yellow (not a brown) colour. He states that aristol of recent manufacture is probably less contaminated with free iodine than the earlier specimens.

Apart, therefore, from the details of its constitution, it is in all cases expected to be a thymol derivative. I propose to show in the following that this is not always the case, and to infer that it frequently is not so:—

A sample of aristol was procured through ordinary wholesale channels. It occurred as a pinkish, yellow-brown, light, pulverulent substance, with thymol-like odour. When heated in air oven at 100° C. for some time, it lost the greater part of its colour; snd when afterwards heated further, it melted to a brown sticky mass at about 156° C.

A quantity was dissolved in ether, filtered from extraneous matters, recovered, and then air-dried at ordinary temperature for two days. The total iodine was then estimated.

Quantity taken = 0·2128 grm.
Silver iodide found = 0·1621 ,, = 41·16 p.c. iodine.

When deposited from ethereal solution it was found to hold water very tenaciously on account of its glutinous character. It was therefore further dried for ten days, and the iodine again estimated.

Quantity taken = 0·2527 grm.
Silver iodide found = 0·1980 ,, = 42·33 p.c. iodine.

A quantity of the ether-purified aristol was heated in sealed tube with water and copper at about 130° C. for twelve hours. The substance, which on cooling had caked on the sides of the tube and acquired a much lighter colour, was rinsed out. It was collected, powdered moist, and rubbed down with water, then treated with weak solution of potash in order to dissolve out any "thymol" or true substituted "iodo-thymols" which might have existed in the original or been formed as the result of the treatment, and also any traces of free iodine, and finally it was slightly washed with alcohol. It was then dried, dissolved in ether, filtered, recovered, powdered, and treated with absolute alcohol (cold) as long as anything dissolved out; the alcoholic solution was then evaporated down, finally under the air-pump, as it began to show signs of free iodine at the dry edges. Colour, yellowish, and of somewhat sticky character.

Total iodine of the alcohol-soluble portion:—
Quantity taken = 0·1177 grm.
Silver iodide found = 0·0897 ,, = 41·17 p.c. iodine.
Combustion of same:—
Quantity taken = 0·0780 grm.
Water found = 0·0356 ,, = 5·07 p.c. hydrogen.
Carbon dioxide found = 0·1454 ,, = 50·83 ,, carbon.
By difference .. .. = 2·93 ,, oxygen.
Distinct ash.

The remaining portion insoluble in alcohol was dissolved in ether, recovered, powdered, and dried. It was of greyish white colour and pulverulent, melting with decomposition.

Total iodine of the alcohol-insoluble portion:—
Quantity taken = 0·1530 grm.
Silver iodide found = 0·1192 ,, = 42·09 p.c. iodine.
Combustion of same:—
Quantity taken = 0·0886 grm.
Water found = 0·0428 ,, = 5·37 p.c. hydrogen.
Carbon dioxide found = 0·1685 ,, = 51·86 ,, carbon.
Distinct ash, containing both copper and iron.

A quantity of the ether-purified aristol was treated with boiling alcohol as long as anything dissolved out, the alcoholic solutions being filtered off. As the united alcoholic solutions cooled, a whitish substance separated out, the solution retaining its yellowish red colour. This precipitate was filtered off, but when dried the quantity was so little that it was not further examined.

The alcoholic solution was evaporated down, and the residue, which was of a bright yellow colour, powdered and dried.

Total iodine of the alcohol-soluble portion:—
Quantity taken = 0·1930 grm.
Silver iodide found = 0·1621 ,, = 45·38 p.c. iodine.
Combustion of same:—
Quantity taken = 0·1125 grm.
Water found = 0·0494 ,, = 4·87 p.c. hydrogen.
Carbon dioxide found = 0·2006 ,, = 48·62 ,, carbon.

A quantity of the same alcohol-soluble portion was heated in sealed tube with copper and water at about 140° C. The product, after having been taken out and dried, was dissolved out by means of ether, recovered, and dried. Colour, greyish white, and of pulverulent character.

Total iodine of this product:—
Quantity taken = 0·1551 grm.
Silver iodide found = 0·1169 ,, = 40·72 p.c. iodine.

The quantity of "extraneous" iodine in the original was therefore 4·66 per cent. Calculating the carbon and hydrogen in the real substance on the strength of this, we obtain the percentages—Carbon 50·99, hydrogen 5·11. The composition of the real substance was therefore:—

Carbon .. .. .. .. = 50·99
Hydrogen .. .. .. .. = 5·11
Iodine . .. .. .. .. = 40·72
Oxygen .. .. .. .. = 3·18

Those figures agree with those found in the analyses of the alcohol-soluble portion obtained from the total aristol heated in sealed tube, and prove that the compounds then examined were not decomposition products.

The remaining portion of the aristol insoluble in boiling alcohol was dissolved in ether, recovered, powdered, and dried. Colour of a dirty yellowish white.

Total iodine of the alcohol-insoluble portion:—
Quantity taken = 0·1039 grm.
Silver iodide found = 0·0806 ,, = 41·91 p.c. iodine.
Combustion of same:—
Quantity taken = 0·1140 grm.
Water found = 0·0518 ,, = 5·13 p.c. hydrogen.
Carbon dioxide found = 0·2166 ,, = 51·81 ,, carbon.
Ash .. .. .. .. .. .. = 0·80 ,,

Another sample was procured at a later period, and after purifying by solution in ether and filtering, the recovered substance was air-dried for ten days and the total iodine estimated.

Quantity taken = 0·2000 grm.
Silver iodide found = 0·1674 ,, = 45·20 p.c. iodine.

A combustion was also made of the same.

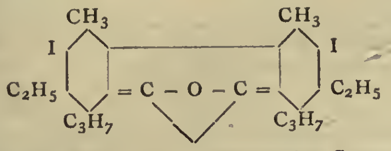
Quantity taken = 0·1389 grm.
Water found = 0·0623 ,, = 4·98 p.c. hydrogen.
Carbon dioxide found = 0·2459 ,, = 48·34 ,, carbon.

The physical properties and appearance of this sample were the same as those of the sample before examined. Those results show how variable the total iodine percentage of commercial samples is. This becomes the more important when we consider that the large differences depend on a portion of the iodine, which exists in a state relatively free, and therefore in a very active state relative to the animal economy.

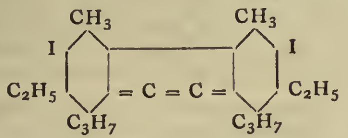
It is quite apparent from the above analyses that those specimens of aristol were not prepared by the action of iodine on thymol in aqueous alkaline solution, and probably were not prepared from thymol in any form.

The alcohol-soluble portion may be represented by the formula $C_{26}H_{30}I_2O$, and the alcohol-insoluble portion by $C_{26}H_{30}I_2$, or constitutionally thus:—(see next column).

In a paper read at the Pharmaceutical Meeting of the Philadelphia College of Pharmacy, March 17, 1891, by George M. Beringer, Ph.G., and reprinted in the *Pharm. Journ.* of June 13, 1891, p. 1135, entitled "What is Aristol, and How is it Manufactured?" the author gives the results of an examination of a sample supplied by the Farben Fabriken Company, of Elberfeld. The physical characters of the substance there enumerated agree generally with those observed in the sample whose analyses I have submitted. The total iodine percentage reported by him (Carius's method), namely, 41·87, agrees with that given by me.



Theoretical .. .. .. { 50·98 = C = 52·35
4·90 = H = 5·02
41·50 = I = 42·63
2·62 = O = 00·00



"Goldman states that aristol is di-iodo-dithymol, $C_{20}H_{24}I_2O_2$, containing 45·8 per cent of iodine. Accepting his formula, there should be by calculation 46·15 per cent of iodine. But the manufacturers drying the product at a low temperature to prevent decomposition, there must be some water retained, and the loss on heating on the water-bath, determined above as about 6·4 per cent, must be due mainly to water. Allowing two equivalents of water to be in combination, there would be present 6·14 per cent of water and 41·96 per cent of iodine, figures that closely agree with those results obtained by me. . . . From these experiments we are compelled to accept the statement that aristol is a biniodide of thymol, in which the hydrogen of the hydroxyl groups is replaced by iodine, and is represented by the formula $C_{20}H_{24}I_2O_2.2H_2O$."

The author repeated the reduction experiments of Messinger and Pickersgill, and obtained a product which corresponded fairly well with the properties assigned to dithymol, and possessed a peculiar odour of thymol almost phenol-like. (The method of reduction referred to—*Berichte*, xxiii., p. 2761—consisted in subjecting an ethereal solution to the action of an alcoholic solution of potash and zinc-dust at an elevated temperature).

The assumption as to the existence of 6·14 per cent of water, given as an explanation of the loss of weight on heating, is in all liklihood entirely erroneous; at all events, the assumption as to the existence of two molecules of water in the compound is. I have little doubt but that what was lost on heating was principally iodine. It is extremely likely that the sample was of the same ultimate composition as the one whose full analyses I have given, and that the reduction product was not dithymol.

(To be continued).

## NOTICES OF BOOKS.

*A Standard Dictionary of the English Language.* New York: Funk and Wagnall's Company.

The matter before us is not the complete work, nor yet a volume or part, but a number of sample pages calculated to show the characteristic features of this great publication. Our opinion, founded on these specimens, is most favourable. It is, indeed, a bold undertaking to compress into a single volume such an extent and variety of knowledge on English words, their uses and their abuses. We naturally turn first to those departments in which our ordinary dictionaries have been the poorest—the terminology of the various sciences and of the industrial arts.

A very useful and gratifying feature is the exact definition of colours. A table will appear "containing the analysis of several hundred shades and tints now before the public in various forms." This is an improvement the more needful since, in addition to the correct names used by physicists, chemists, colour-makers, biologists, and dyers, we are often perplexed by the terms invented by drapers and modistes.

The article "element" is most satisfactory, as all the different acceptations—chiefly scientific—in which the word can be used are clearly explained.

The table of chemical elements must meet with the approval of every competent judge. It is arranged on the periodic system, and gives in parallel columns the name of each element, its derivation, symbol, atomic weight, specific gravity, melting-point, valence, date of discovery, discoverer, and sources.

The illustrated articles on "bacteria," on "cells," and on bone are certainly all that can be reasonably expected where space is necessarily limited. From the passages mentioned we may conclude that scientific terms generally will be most ably dealt with.

But in other respects the "Standard" must command approval. We may particularly note the instances of "faulty pronunciation and diction" selected from different parts of the work. The Cockneyism of dropping the letter *r* or inserting it where it has no business, does not escape due censure. The use of "quite" as a synonym for "very," or as "awful" as a general emphasizing appendage is, we fear, increasingly common on both sides of the Atlantic. We are rather surprised to find "nasty" as a synonym for "disagreeable" objected to by the editor of that department.

In giving the meanings of any word, the "Standard" places *first* the acceptation which it generally bears at the present day. Then follow more meanings, and lastly such as are obsolescent or obsolete. This is certainly not the logical order, but it is the most practical. The quotations used to verify the meanings of words bear not merely the name of the author, but the volume, page, and edition whence they are taken. This is a decided improvement on the plan which has hitherto been generally followed.

Synonyms, autonyms, and the correct use of prepositions, so far as we can judge from the specimens before us, have been judiciously dealt with.

There is a singular impartiality shown in the selection and treatment of the subjects. Homœopathy, phrenology, the selective system of medicine, and socialism are assigned to special editors. We have every confidence that the work will tend to arrest a process which is already felt—the fractionation of the English language into a number of discordant dialects. If it can do anything to heal the cancer of slang so much the better.

*Alembic Club Reprints. No. 3. Experiments on Air.* (Papers published in the *Philosophical Transactions*). By The Hon. Henry Cavendish, F.R.S. (1784—1785). Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1893.

The first of these two papers, as we learn from the preface, contains Cavendish's account of his investigations on the composition of water. All chemists are probably aware that prior to the year 1780 water ranked as an element. During the next decade it was proved to be an oxide of hydrogen. But both the exact date and the authorship of this capital discovery have been warmly contested.

In the "Elements of Chemistry" (Edition VII.), by Turner, edited by Liebig and Gregory, the composition of water is said to have been discovered by Cavendish, no date being given. In the English version of Gmelin's great work the discovery is said to have been made by Cavendish and Watt, in 1781. In the "Dictionary of Science, Literature, and Art," by Brande and Cox, we find the date of the discovery given as 1786 and 1787, and its authorship ascribed to "Watt and Cavendish." The actual date of the paper read by Cavendish before the Royal Society is here given as 1784. We thus approach the once famous "Water Controversy," *i.e.*, the question whether Cavendish or Watt was the original and true discoverer of the nature of water? It is certain that these two *savans* were not working in concert, as the language of some of the text-books might lead the reader to suppose. Watt was certainly, as we see from p. 25 of the work before us, engaged with subjects bearing upon the composition of water. But no one who has formed an accurate idea of the ways of Cavendish can for a moment suspect him of seeking to appropriate any credit due to another. He took little pains to establish his own claims or to take date. Some of his researches have only been published late in the present century, and of others no record has been left, so that their existence is merely a matter of inference.

Two "interpolations" were made in the paper by Sir Charles Blagdon, Cavendish's secretary (p. 20 and p. 25), and Cavendish himself made an addition after the paper had been read, but before it had been printed (p. 35).

The phlogistian nomenclature used by Cavendish has been retained of necessity.

This little book will be very useful to all who are studying the history of præ Lavoisian chemistry.

*A Course of Practical Chemistry and Qualitative Chemical Analysis.* By the late W. G. Valentin, F.C.S. Edited and Revised by W. R. Hodgkinson, Ph.D., F.R.S.E., F.C.S., F.G.S., &c., Jodrell Scholar and formerly Senior Demonstrator and Lecturer in the Normal School of Science and Royal School of Mines; Professor of Chemistry and Physics in the Royal Military Academy and Artillery College, Woolwich. Eighth Edition. London: J. and A. Churchill. 1893.

This work is doubtless well known to many of our readers in its original form; but it now appears before us in a modified, and, in our opinion, a much improved state. It now brings forward the spectroscopic characteristics of the elements much more prominently than we find in ordinary analytical manuals

A most important section is Appendix I., giving the reactions of the rare elements and directions for their separation into groups. This section will be the more welcome to the earnest student as in too many text-books the rare elements are either ignored altogether or at most considered in a very perfunctory manner.

Appendix II. contains a judicious selection of quantitative exercises.

Appendix III. treats of the non-metallic elements. Under Carbon we find the interesting remark, "There is just a doubt whether diamond is carbon only."

In Appendix IV. we find given the reactions of morphine, narcotine, quinine, cinchonine, strychnine, and brucine, with the divisions of the alkaloids into groups.

In looking over the list of reagents we find mention of methylated spirit. It is doubtful whether the passage was not written before the late mischievous tampering with this useful solvent. It can, of course, be obtained, theoretically speaking, in its old form, but no inconsiderable length of red tape has to be uncoiled, and the laboratory of the applicant is exposed to visits from the exciseman.

A peculiarity of this work is that in it formulæ are much more frequently used than in most analytical manuals. At the end of most of the sections and paragraphs we encounter a series of questions, in some cases as many as twenty-five.

The book ought, we think, to form one of the few elementary treatises to be recommended for a student's book-shelves.

*A B C Five-figure Logarithms for General Use.* By C. J. Woodward, B.Sc. London: E. and F. N. Spon. Birmingham: Cornish Bros. 1893.

Some years ago the author published his "A B C Five-figure Logarithms," containing mantissæ of numbers only. The work was found useful, and met consequently with a favourable reception; but immediately after its appearance it was suggested that to many persons who have numerous calculations to make it would be a convenience to have logarithms of arc functions arranged on a similar principle. This task has been accordingly undertaken, and is now submitted to the public. There are subjoined examples referring to plane and spherical trigonometry, navigation, nautical astronomy, and crystallography.

We have no doubt that this handy volume will prove a boon to the increasing number of persons who have to make incessant use of calculations.

## CORRESPONDENCE.

### PREPARATION OF HYDROGEN.

*To the Editor of the Chemical News.*

Sir,—I have recently observed that, by the addition of a few drops of a solution of cobalt nitrate to the acid and zinc in a hydrogen apparatus, the rate of evolution of hydrogen is enormously accelerated, especially at the beginning of the reaction. The action is the same with either hydrochloric or sulphuric acid, and a couple of drops of solution of cobalt nitrate will suffice for a large quantity of acid.

This action does not seem to have been noticed before; it should be useful in the rapid preparation of hydrogen in the laboratory.

Most of the cobalt nitrate, if not all, is quite unaltered; there appears to be a very thin film of cobalt deposited on the zinc, which probably acts with the zinc as a voltaic couple, but the amount of cobalt deposited appears to be too small to weigh.

A solution of a nickel salt exerts a similar action.—I am, &c.,

John Ball.

Royal College of Science,
South Kensington, Oct. 6, 1893.

### ARRANGEMENT OF CHEMICAL LECTURES.

*To the Editor of the Chemical News.*

Sir,—There is no douht that lectures on chemistry, in which the elements are treated of in the groups of the periodic system, so as to exhibit the characters connecting the members of a group and the points of difference and connection between one group and another, is an excellent plan, especially with students not exactly beginners.

It was tried with classes of science teachers attending the summer courses at South Kensington as early, I think, as 1879, and was continued in following years with undoubted success.

Even with students quite fresh to the subject I find it best to begin this systematic treatment of the elements after one or two preliminary lectures on the "ways" of chemical action and a very short historical outline.

The results with students who have received a proper mathematical training is very striking compared to when the "metals and non-metals" are treated of as disconnected things.—I am, &c.,

W. R. Hodgkinson.

Artillery College, Woolwich,
Oct. 9. 1893.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 13, September 25, 1893.

**Spectroscopic Observations made at the Observatory of Mont Blanc, Sept. 14 and 15, 1893.**—J. Janssen.—The chief object of the observations was the question of the presence of oxygen in the solar atmospheres. The instrument used—a Rowland's grating spectroscope—showed all the known details of group B. It is found that the double lines, the totality of which constitutes the group B, decrease progressively in intensity as their wave-length decreases. At the level of the sea the maps of B show, in addition to the head ray, thirteen or fourteen double lines. At Chamounix, at 1050 metres, the thirteenth is less easy to distinguish. At the Grand-Mulets (3050) metres), we can recognise only from the tenth to the twelfth, and on the summit of Mont Blanc the author could not go beyond the eighth. If we compare these results with tubes full of oxygen, we may infer the total disappearance of group B at the limits of the atmosphere.

**Action of the Electric Arc upon Diamonds, Amorphous Boron, and Crystalline Silicon.**—Henri Moissan.—As soon as the temperature is sufficiently high, the diamond sprouts without melting, and is covered with black masses entirely formed of graphite. After the experiment the graphite has the form of hexagonal laminæ, easily converted into graphitic oxide by treatment with a mixture of potassium chlorate and nitric acid. The stable form of carbon is graphite. If pure amorphous boron is placed in the electric arc, the boron becomes red and is surrounded with an extensive green halo, and then disappears without any phenomena of fusion. After the experiment we find at the extremity of the electrode black masses of a melted appearance presenting some crystalline points formed of a carbon boride. If crystalline silicon is placed between the two electrodes, it enters into fusion and then into true ebullition. When the electrodes are cold we find at their extremity, among the graphite which has been formed, pale green crystals of carbon silicide. Hence it is seen that boron and silicon readily combine with carbon at the temperature of the arc.

**Preparation and Properties of Crystalline Carbon Silicide.**—Henri Moissan.—This compound may be obtained either by direct combination at a temperature between 1200° and 1400° or by crystallisation in melted iron, or on reducing silica by carbon, or by allowing the vapours of the two elements to come in contact. Crystalline carbon silicide is a remarkably stable compound; it is colourless and reacts strongly upon polarised light. Its specific gravity is 3·12. It is hard enough to scratch ruby. It is not affected by oxygen or sulphur at 1000°. It is attacked by a current of chlorine at 1200°; potassium nitrate and chlorate in a melted state have no effect. It is the same with boiling sulphuric acid, hydrochloric acid, and nitric acid, aqua regia, and the mixture of monohydrated nitric acid and hydrofluoric acid. Caustic potassa in fusion disaggregates this compound, and ultimately dissolves it if heated to dull redness for an hour, yielding potassium carbonate and silicate. It yields on analysis 69·70 per cent silicon and 30 per cent carbon, corresponding to the formula $SiO$.

**A Glucoside of the Iris.**—F. Tiemann and G. de Laire.—The glucoside $C_{27}H_{26}O_{13}$, obtained from the roots of the iris, crystallises in fine white needles, which the authors name iridine. This substance, if heated under pressure in sulphuric acid diluted with dilute alcohol, is split up into glucose and a crystalline body, which the authors name irigenine. This substance crystallises from absolute alcohol in yellowish white rhombohedra, melting at 186°. Irigenine forms alcoholic ethers, and gives rise to two series of acid ethers. If submitted to the action of alkaline hydrates it takes up three molecules of water, and is then separated into three substances—formic acid, an acid phenol which the authors name iridic acid, and a phenol which they call iretol. Iridic acid has the composition $C_{10}H_{12}O_5$, whilst iretol is $C_7H_8O_4$.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 3.

**A Support for the Nitrometer.**—Foehr (*Chemiker Zeitung*).—This instrument cannot be intelligibly described without the accompanying illustration.

**A Modification of the Refrigerator with a Bulb-tube.**—Greiner and Friedrichs (*Zeit. fur Angew. Chemie*).—The modification consists in substituting a Liebig-Mohr glass jacket for the bulb-tube, so that the apparatus approaches very closely to an arrangement recently patented by another inventor.

**Lamps for Sodium Light.**—H. E. J. G. du Bois (*Zeitschrift fur Instrumentenkunde*).—The author uses a Linnemann burner, in the flame of which he introduces a soda rod. The rods are preferably 0·4 c.m. in diameter and 12 to 15 c.m. in length. They are made of sodium bicarbonate, sodium bromide, and tragacanth.

**Argand Lamp for the Alternate Production of White and Monochromatic Light.**—E. Pringsheim (*Wiedemann's Annalen*).—A T-tube is inserted in the flexible tube, connecting the gas pipe to the lamp and also communicating with a pulveriser containing solution of common salt. When the pulveriser is not in action the lamp gives a white light.

**Attackability of Platinum and its Iridium Alloys by Sulphuric Acid.**—Heraeus (*Zeit. Angew. Chemie*).—Already inserted.

**Durability of Standard Solutions of Permanganate.**—Bruno Grützner.—The author's experiments prove that a solution of 1 : 1000 underwent no change on exposure to diffused day-light for a year, and in one year and a half only to the extent of 2·61 per cent. In a blackened glass the loss in one year and a half was only 0·94 per cent. The results with a 0·3 per cent solution were still more favourable.

**Preservation of Sodium.**—W. Vaubel (*Zeitschrift fur Angewandte Chemie*) and Merry (Chemical News).

**De-arsenising Chamber Acid.**—Le Roy W. McCay (*Chemiker Zeitung*).—The author proposes to treat the acid with sulphuretted hydrogen at 100° and under pressure.

**Test for Cerium Oxide.**—P. C. Plugge.—*Archiv. der Pharmacie.*

**Detection of Free Salicylic Acid in Salicylic Aldehyd and Salicylic Methyl Ether.**—A. Schneegans and J. E. Gerock (*Journ. de Pharmacie d'Alsace Lorraine*).—The authors have observed that the violet colour produced by solutions of salicylic aldehyd and salicylic methyl ether with ferric salts diaappears on the addition of ethyl, chloroform, amylic alcohol, acetic ether, carbon disulphide, petroleum ether, paraffin oil, benzene, toluene, or xylene, whilst the same colour produced by salicylic acid is permanent.

**Determination of Creosote.**—A. Schlicht (*Pharm. Zeitung*).—The author shakes out the solution of the creosote with ether saturated with water, and calculates the proportion of creosote from the specific gravity of the ether-creosote solution.

**Examination of Ether.** — C. Traub (*Schweitzer Wochenschrift fur Pharmacie*).—Good ether in contact with potassium hydroxide should undergo no change for twelve hours. The ether should be repeatedly examined for its odour upon blotting-paper. Pure ether dissolves in sulphuric acid without colour if added carefully and kept well cooled.

**Examination of Ammonium Chloride for Pyrogenous Substances.**—O. Schobert (*Pharm. Zeitung*).—According to the author, if 50 c.c. of a 5 per cent solution of ammonium chloride is mixed with 1 c.c. of a solution of permanganate, the red colour must not disappear within ten minutes.

**Determination of Cyanogen in Laming's Mass.**

**The Use of Sodium Nitro-prusside as a Reagent for Aldehyds and Ketones.**—Béla von Bittó (*Liebig's Annalen*).—The author draws from his experiments the general conclusion that the reaction in the aldehyds and ketones belonging to the fatty series always takes place when the aldehyd group CHO or the carbonyl group CO is directly connected with at least one group consisting only of carbon and hydrogen.

**Reactions of the Aldehyds and Ketones with Aromatic Nitro-compounds.**—Béla von Bittó.—The author reports with reference to the reactions with sodium nitro-prusside considered in the foregoing paper. Experiments with other nitrogen compounds, all of which had a negative result, rendered it probable that the reaction is occasioned by the nitroso-group (*Annalen der Chemie*).

**The Uses of the Calorimetric Bomb.**—M. Berthelot.—From the *Comptes Rendus*, cxv., p. 201.

**The Elementary Analysis of Acetyl Fluoride.**—M. Meslans.—From the *Comptes Rendus*, cxiv., p. 1069.

**Determination of Sulphur in Organic Substances.**—A. Angeli (*Gazzetta Chimica* and *Journal of Chemical Society*).—Many organic substances if heated with nitric acid in a sealed tube, as in the method of Carius, are decomposed with much difficulty. The oxidation is much accelerated or completed by an addition of bromine.

**A Method for Determining Organic Substances by Oxidation with Potassium Chromate and Nitric Acid.** — H. Heidenheim (*Der Techniker*). — This paper requires the accompanying illustration.

**The Separation of Oleic Acid from Stearic and Palmitic Acids.** — Otto Hehner. — From the *Analyst*, xvii., 181.

**Determination of Iodoform.** — M. Greshof. — The author's method depends on the transformation—

$$CHI_3+3AgNO_3+H_2O=3AgI+3HNO_3+CO_2.$$

Whilst Greshof worked on an aqueous solution, Ritsert (*Pharm. Central Halle*, xxxi., 610) modified the process by dissolving the iodoform in alcohol or ether-alcohol, acidulating with nitric acid, and titrating with silver nitrate at the heat of the water-bath. Greshof (*Pharm. Central Halle*, xxxii., 232) replying, considers it more advantageous to work according to his original method.

**Influence of Mouldiness on the Composition of Bread.**—Th. Dietrich.—The moulds grow at the expense of the carbohydrates of bread. Hence mouldy bread is relatively richer in proteine compounds.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Bleaching Oils.**—I read lately that silicate of soda was much used in the bleaching of oil. Could any of your correspondents tell me *how* it is so employed? Would it answer for bleaching fish oils?—J. D. Johnstone.

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## THE GASES "ENCLOSED" IN COAL DUST.*

By P. PHILLIPS BEDSON, D.Sc.

THE investigations of Professor von Meyer (*Journ. Prakt. Chem.*, [2], v., 146—183 and 407—416; also *Journ. Chem. Soc.*, x., 798) and of Mr. W. J. Thomas (*Journ. Chem. Soc.*, 1875 and 1876) have made us familiar with the fact that coal contains occluded or enclosed gases and with the general composition of the gases yielded by different varieties of coal. These gases consist, as a rule, of mixtures of carbon dioxide, oxygen, nitrogen, and marsh gas; in some cases von Meyer observed certain varieties of weathered coal to contain, in addition to marsh gas, some olefine hydrocarbons, and also denser members of the paraffin series of hydrocarbons, and further, the gases obtained by W. J. Thomas from cannel and jet were also found to contain similar hydrocarbons.

In a paper read some five or six years ago before the North of England Institute of Mining and Mechanical Engineers, I gave an account of the results of experiments made by applying Thomas's method of extracting the gases from coal, to coal dust. These experiments demonstrated that the coal dust under examination, when heated at 100° C. *in vacuo* for several hours, yielded from one-half to eight-tenths of its volume of gas. The gas obtained in this manner proved on analysis to contain carbon dioxide, oxygen, nitrogen, some olefines and hydrocarbons of the paraffin series. In analysing these gases I was, by reason of the lack of suitable laboratory accommodation, compelled to use the apparatus, &c., devised by Hempel, which, whilst admirably adapted for technical purposes, leaves much to be wished for in determining the nature and amount of the combustible gas left, after removal by absorbents, of carbon dioxide, oxygen, and olefines. Still, the results obtained showed conclusively that the combustible gas left after the absorption of the gases named was not simply marsh gas.

In determining the nature of this combustible gas, a measured volume of the residue left after the removal of the gases mentioned was mixed with oxygen and the mixture exploded. From the volume of carbon dioxide produced, the contraction resulting from the explosion, the volume of oxygen used in the combustion, and the volume of nitrogen present, the proportion of combustible gas present was determined, and, assuming it to be a paraffin hydrocarbon, its probable composition was calculated by the aid of the following equation—

$$C_nH_{2n+2}+(3n+1)O=nCO_2+n+1(H_2O).$$

From which it is seen that 2 vols. of $C_nH_{2n+2}$ would produce $2_n$ vols. of $CO_2$, give a contraction of $(n+3)$ vols., and would require $(3n+1)$ vols. of oxygen. The values found for "$n$" from the data provided by the explosions and the above relationships indicated the undoubted presence of higher members of the paraffin series; the values for $n$ found for the gases from one sample of the dust being 2·78, and 2·42 in another case.

The coal dust with which these experiments were made was that collected on the screens at the Ryhope Colliery, in the county of Durham, and the investigation was undertaken with the hope of finding an explanation of the observation frequently made at this colliery that the cloud of dust produced in screening this special coal would often fire at the lamps used for lighting the screen, and in this manner produce a species of explosion.

Since the publication of these results I have repeated the examination of this dust, and in the analysis of the gases have employed more exact and refined methods, using for that purpose the apparatus devised by the late Professor Dittmar. Further, in extracting the gases I attempted to effect a species of fractionation of the combustible constituents by performing the extraction at different temperatures. For this purpose, some 670 grms. of the dust were placed in a bottle and attached to the mercury pump, and after the air had been completely removed, the coal dust was heated by means of a water-bath for some twenty days at 30° C.; the gas produced was drawn off and measured. The temperature was then raised to 50° C., which was maintained for ten days; in this way a second quantity of gas was obtained. A third extraction was made by heating at 60° for another ten days, a fourth by heating at 60—80° C. for seven days, and finally a fifth by heating at 100° for some nine hours.

In this way the following volumes of gas were obtained:—

| | | | |
|---|---|---|---|
| First extraction | (30° C.).. .. | 100·9 | c.c. at N.T.P. |
| Second ,, | (50° C.).. .. | 160·6 | ,, ,, |
| Third ,, | (60° C.).. .. | 116·3 | ,, ,, |
| Fourth ,, | (60—80° C.).. | 286 | ,, ,, |
| Fifth ,, | (100° C.) .. | 89·5 | ,, ,, |
| | | 753·3 | |

This volume represents 112·4 c.c. of gas N.T.P. for every 100 grms of coal dust.

The following Table gives the results of the analysis of the several samples of gas:—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon dioxide .. .. | 5·77 | 8·34 | 12·12 | 27·35 | 20·8 |
| Oxygen .. .. .. .. | 9·33 | 7·31 | 5·35 | 0·56 | 4·16 |
| Carbon monoxide .. | — | — | — | 1·68 | 2·34 |
| Olefines ($C_nH_{2n}$).. .. | — | 0·39 | 0·77 | 2·14 | 4·74 |
| Paraffins ($C_nH_{m+2}$) .. | 3·16 | 4·95 | 9·39 | 31·86 | 29·8 |
| Nitrogen .. .. .. | 81·6 | 79·01 | 72·37 | 35·70 | 38·16 |
| | 99·86 | 100·00 | 100·00 | 99·29 | 100·00 |
| Values for $n$ in formula $C_nH_{2n+2}$ .. .. $n=$ | 2·1 | 2·2 | 2·1 | 2·3 | 2·8 |

The changes to be observed in the composition of these gases given off at different temperatures are the gradual increase in the proportion of carbon dioxide and a diminution in the proportion of oxygen. This does not obtain with the gases produced at the highest temperature, and that is doubtless due to the fact that at this stage it was necessary to dismount the apparatus, by which the dust was brought into contact with the air. It will be further noted that whilst some combustible gas is given off at 30° C., the proportion increases with rise in temperature of the bath, the greater portion coming off between 80° and 100°, at which temperature the olefines and carbon monoxide make their appearance. The nature of the paraffin hydrocarbons, as shown by the value for $n$ in the formula $C_nH_{2n+2}$, does not appear to suffer much change until at 100°, when the value corresponds very nearly to propane ($C_3H_8$). Although the analysis of a mixture of such hydrocarbons does not enable us to determine the nature of the components, still there is in the above values for $n$ a sufficient indication that the lighter gases of this series are the first to come away when the dust is heated *in vacuo*.

In this connection the question naturally arises—What is the nature of the gases enclosed in the coal from which this dust is produced? The solution of this question has been attempted by one of my students, Mr. W. McConnell, jun., who has examined the coal taken fresh from the same seam (the Hutton seam, Ryhope Colliery), and the results may be stated briefly as follows. 100 grms. of coal, heated *in vacuo* at 100° C., give 818 c.c. of gas at N.T.P. of the following composition.

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* Read before the British Association (Section B), Nottingham Meeting, 1893.

| | Volume. |
|---|---|
| Carbon dioxide .. .. .. .. | 0·7 |
| Oxygen .. .. .. .. .. .. | 9·4 |
| Carbon monoxide .. .. .. | 0·1 |
| Olefines .. .. .. .. .. | 0·0 |
| Marsh gas .. .. .. .. .. | 16·6 |
| Nitrogen .. .. .. .. .. .. | 73·0 |
| | 99·8 |

The paraffin hydrocarbon is here stated to be marsh gas, as the results of the analysis indicated this to be the case. The coal, after the gases had been extracted, was reduced to a fine powder, and the crushed coal again heated at 100° C. in an exhausted vessel attached to the air-pump. In this manner, from 208 grms. of the crushed coal, 109 c.c. of gas at N.T.P. were obtained, the analysis of which proved it to have the following composition:—

| | Volume. |
|---|---|
| Carbon dioxide .. .. .. | 0·85 |
| Oxygen .. .. .. .. .. | 6·95 |
| Carbon monoxide .. .. | trace |
| Olefines.. .. .. .. .. .. | 1·10 |
| Paraffins ($C_nH_{2n+2}$) .. .. | 17·90 |
| Nitrogen .. .. .. .. | 73·20 |
| | 100·00 |

The results of the determination of the composition of the paraffin give a value of 2·06 for *n*; showing the existence here of combustible gases similar to those obtained from the dust collected in the screens.

Further, Mr. McConnell has found that after heating the coal *in vacuo* at temperatures as high as 180° C., until it ceased to give off any gas, the coal, on crushing to a powder and heating again under reduced pressure at 100°, gave a further quantity of gas, which contained 39·7 per cent of paraffin hydrocarbons; the results of the combustion of which show the presence of some of the higher members of the paraffin series.

During the past two years Mr. McConnell (Royal Exhibition Scholar) has been engaged in the chemical laboratory of the Durham College of Science, in the examination of the gases "enclosed in" different coal dusts produced in the working of coal raised in the Northumberland and Durham coal fields. The detailed results of this investigation will be published shortly. I may, however, state that some of the dusts examined have been found to yield mixtures of carbon dioxide, oxygen, and nitrogen only. The coal from which these dusts were produced gave mixtures of a similar composition. Other varieties of dust were found to contain a small quantity of combustible gas in addition; whilst a third class was found to resemble the dust from the Ryhope Colliery, with the nature of the gases from which I have already dealt, and the chief point of interest in which is the existence among the combustible gases of such hydrocarbons as ethane and propane. The coals from which this third class of dusts are obtained have been proved to give occluded gases, similar in composition to the gas obtained from the Ryhope coal; the combustible constituent being marsh gas only. Further, these coals themselves, after the occluded gases had been removed by heating *in vacuo* at 100° C., gave, on crushing and heating the powdered coal at 100° *in vacuo*, a further quantity of gas containing some of the higher members of the paraffin series of hydrocarbons.

These results have an interest beyond the demonstration of the fact that the denser hydrocarbons are more firmly held by the coal substance than the lighter marsh gas; and that in the working of the coal the reduction to a fine powder, such as coal dust, must by free exposure to the air allow ample opportunity for a ready diffusion of the marsh gas; the denser hydrocarbons being retained by the particles of coal. Again, the existence of such enclosed gases in coal dust show that in considering the part played by coal dust in forming explosive mixtures with air, we may have to deal with a variety of dust which might readily yield such hydrocarbons, as those found in the gases enclosed in the dusts examined by Mr. McConnell and myself. For these gases differ from marsh gas not only in the proportion required to form an explosive mixture with air; thus whilst 1 volume of marsh gas would require 10 volumes of air for its complete combustion, 1 volume of the hydrocarbons found in the Ryhope coal dust would require 23 volumes of air; or, in other words, whilst 9·3 per cent of marsh gas is required to form the most explosive mixture with air, about 4 per cent only of the combustible gas obtained from the Ryhope coal dust would be required. But the difference between marsh gas and its next homologues is seen again in the temperature required to ignite such explosive mixtures, for it has been recently shown by Victor Meyer that the temperature of ignition of explosive mixtures of oxygen and ethane is lower than that of marsh gas and oxygen.

These facts point to the ready inflammability and the sensitiveness of dusts containing such hydrocarbons—a conclusion borne out by the ignition of the coal dust on the screens at the Ryhope Colliery—a fact which led me originally to investigate this subject; and, further, the Austrian Fire-damp Commission has from the experiments with coal dust been led to the conclusion that the sensitiveness of dusts increases with the proportion of easily inflammable hydrocarbons, especially with the amount of ethane liberated at 100° C. and with the dryness of the dust.

There are doubtless other factors which contribute to the ready inflammability and sensitiveness of a coal dust, and one can easily understand how this would be contributed to by the fineness of subdivision and again by the air which the coal may absorb by long-continued exposure in an air current.

## THE APPLICATION OF ELECTROLYSIS TO QUALITATIVE ANALYSIS.*

By CHARLES A. KOHN, Ph.D., B.Sc.,
Lecturer on Organic Chemistry, University College, Liverpool.

The first application of electrolysis to chemical analysis was made by Gaultier de Claubry in 1850, who employed the electric current for the isolation of poisonous metals, using platinum electrodes, on which the deposition of the metal took place.

Other early workers followed in this direction, and in 1861 C. L. Bloxam published two papers on "The Application of Electrolysis to the Detection of Poisonous Metals in Mixtures of Organic Matters" (*Journ. Chem. Soc.*, xiii., 12 and 338). The author appears to have made extensive use of the methods described in these papers, and which have reference to the detection of arsenic, antimony, mercury, bismuth, and copper. The electrolysis was effected in acidulated solutions, from which the arsenic was evolved as hydride, whilst the other metals were deposited in the metallic state upon the cathode and subsequently tested, after dissolving, by the usual reactions.

Since the publication of these results, the advances in electrolytic analysis have reference to quantitative methods only, and the advantage of these latter for qualitative work has been to some extent overlooked.

Within the last twelve years Classen and his pupils have placed a number of electrolytic methods for the determination and separation of metals in the hands of chemists—methods which have been added to by the labours of E. F. Smith, Vortmann, and others.

These methods are of special value when applied to qualitative analysis in cases of medical or medico-legal

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* A Paper read before the British Association (Section B), Nottingham Meeting, 1893.

inquiry. They are not supposed to supersede in any way the ordinary methods of qualitative analysis, but to serve as a final and crucial means of identification, and thus render it possible to detect very small quantities of the substances in question with great accuracy. As such, they fulfil the required conditions admirably, being readily carried out, comparatively free from contamination with impure reagents, and capable of being rendered approximately quantitative whenever desired.

The method devised by Bloxam for the detection of arsenic, in which all fear of contamination with impure zinc is avoided, has been elaborated by Wolff (*Journ. Soc. Chem. Ind.*, 1887, p. 147), who has succeeded in detecting 0·00001 grm. of arsenious acid by this means.

It is in connection with the most important of the remaining mineral poisons that I have examined the applicability of these electrolytic methods, viz., antimony, mercury, lead, copper, and cadmium.

### *Antimony.*

The method employed in the case of antimony is that adopted in its quantitative estimation by means of electrolysis, a method which ensures a complete separation from those metals with which it is precipitated in the ordinary course of analysis, arsenic and tin. This fact is of considerable importance in reference to the special objects for which these methods have been worked out.

The precipitated sulphide is dissolved in potassium sulphide, and the resulting solution, after warming with a little hydrogen peroxide to decolourise any polysulphides that may be present, electrolysed with a current of 1·5—2 c.c. of electrolytic gas per minute (10·436 c.c. at 0° and 760 m.m. = 1 ampère), when the antimony is deposited as metal upon the negative electrode. One part of antimony (as metal) in 1,500,000 parts of solution may be thus detected—a reaction thirty times more delicate than the deposition by means of zinc and platinum. The stain on the cathode, which latter is best used in the form of a piece of platinum foil about 1 c.m. in diameter, is distinct even with a solution containing $\frac{1}{28}$ m.grm. of antimony, and by carefully evaporating a little ammonium sulphide on the foil, or by dissolving the stain in hot hydrochloric acid and then passing a few bubbles of sulphuretted hydrogen gas into the solution, the orange-coloured sulphide is obtained as a satisfactory confirmatory test. The detection of 0·0001 grm. of metal can be fully relied on under all conditions, and one hour is sufficient to completely precipitate such small quantities.

### *Mercury.*

Mercury is best separated from its nitric acid solution on a small closely-wound spiral of platinum wire. The solution to be tested is acidified with nitric acid and electrolysed with a current of 4—5 c.c. (c.c. refer to c.c. of electrolytic gas per minute). The deposition is effected in half an hour. The deposited metal is removed from the spiral by heating the latter gently in a test-tube, when the mercury forms in characteristic globules on the upper portion of the tube. As a confirmatory and very characteristic test, a crystal of iodine is dropped into the tube, and the whole allowed to stand for a short time, when the presence of mercury is indicated by the formation of the red iodide. 0·0001 grm. of mercury in 150 c.c. of solution can be clearly detected.

Wolff has applied this test under similar conditions, using a special form of apparatus through which the solution to be tested is allowed to pass slowly, and in which a silver-coated iron electrode is employed as the anode.

### *Lead.*

Lead is precipitated either as $PbO_2$ at the anode from a solution containing 10—20 per cent of free nitric acid, or as metal, at the cathode, from an ammonium oxalate solution. In both cases a current of 2 to 3 c.c. suffices to effect the deposition in one hour.

Here, again, 0·0001 grm. of metal in 150 c.c. of solution can be easily detected. With both solutions this amount gives a distinct colouration to the platinum spiral on which the deposition is best effected. As a confirmatory test, the deposited metal is dissolved in acid and tested with sulphuretted hydrogen, or the spiral may be placed in a test-tube and warmed gently with a small crystal of iodine, when the yellow iodide of lead is formed. The latter reaction is very distinct, especially in the case of the peroxide.

Of the above two methods, that in which an ammonium oxalate solution is used is the more delicate, although it cannot be employed quantitatively, owing to the oxidation that takes place on drying. An addition of 1 grm. of ammonium oxalate to the suspected solution is sufficient.

A great advantage of the electrolytic method as a crucial means for the detection of minute quantities of lead lies in the fact that, when the lead is deposited as peroxide from a nitric acid solution, it is completely separated from mercury, copper, cadmium, arsenic, antimony, and iron, none of which are deposited at the anode in this case. Manganese is the only commonly occurring element that behaves similarly.

This method is, therefore, of value for the determination of lead in water, citric and tartaric acids, baking-powders, &c.

If quantitative results for small quantities of lead are required, the best plan is to effect the electrolysis in nitric acid solution, as above, employing a small platinum dish as the anode, to which the deposited peroxide adheres well, and which can be weighed as $PbO_2$ after washing and drying at 110° C. May has suggested (*Zeit. f. Anal. Chem.*, xiv., 344) the ignition of the $PbO_2$ to $PbO$ and final weighing of the latter; but a loss always occurs under these conditions, which increases with the quantity of the peroxide present. This loss amounts to 2—3 per cent of the weight of lead deposited.

### *Copper.*

0·00005 grm. of copper can be very readily detected by electrolysing an acid solution in the usual way. A spiral of platinum wire is employed as the cathode, and the presence of the metal confirmed by dissolving it in a little nitric acid and testing with potassium ferrocyanide.

Quantitative results in solutions containing 0·001 grm. of metal are thus obtained with considerable accuracy, and the method, as in the case of lead, is of use for the detection of minute quantities of the metal in waters. The advantages of electrolysis over the colorimetric methods usually employed in such cases are twofold. In the first place, concentration is not necessary, owing to the delicacy of the test; and, secondly, the erroneous results that are obtained in all colorimetric processes, due to the influence of the varying constituents present in the solution tested on the accuracy of the reaction, are entirely obviated.

### *Cadmium.*

Cadmium is deposited in the metallic state both from potassium cyanide and from potassium oxalate solutions, the former of which is preferable. A current of 0·2 c.c. is sufficient, and 0·0001 grm. of the metal can be thus detected. To confirm, the deposit is dissolved in hydrochloric acid, the solution diluted and treated with sulphuretted hydrogen.

### *Detection of Metallic Poisons in Urine by Means of Electrolysis.*

To apply the above methods in cases of poisoning, the organic matter with which the metals are associated must first be destroyed in the usual way by means of hydrochloric acid and potassium chlorate, and the solutions or precipitates obtained in the ordinary course of analysis then subjected, at suitable stages, to electrolysis. In such cases the advantages of electrolysis lie, again, in the delicacy and reliability of the tests, and also in the fact that the small quantities of organic matter with which the solutions obtained in such cases are contaminated do not interfere with the electrolytic tests as they do with the ordinary wet tests. By passing the current for a longer time than is required for ordinary aqueous solutions the organic matter is decomposed and thus prevented from affecting the reliability of the tests.

The detection of metallic poisons in urine can be directly effected by electrolysis.

The presence of mercury or of copper is detected by acidifying the urine with 2—3 c.c. of nitric acid (conc.) and electrolysing as described. 0·0001 grm. of metal can be detected thus in 30 c.c. of urine, or 1 part in 300,000 of urine.

*Lead* does not separate well as peroxide from urine acidified with nitric acid, but if ammonium oxalate be added the reaction is quite as delicate as in aqueous solution, and 0·0001 grm. of lead can be thus detected.

*Antimony* can be detected directly in urine, according to Chittenden (*Proc. Connecticut Acad. of Science*, viii.), by electrolysis after the addition of 2—3 c.c. of dilute sulphuric acid; but this process was not found satisfactory. The better plan is to first precipitate by sulphuretted hydrogen and then electrolyse as described.

In all these cases it is necessary to pass the current at least twice as long as when aqueous solutions are employed. In twenty-four hours a current of 1—2 c.c. completely decomposes urine, leaving a clear and colourless solution.

A comparison of the delicacy of these tests with the ordinary qualitative tests for antimony, mercury, lead, and copper by means of sulphuretted hydrogen showed that in the case of antimony and of copper the electrolytic tests were one and a half times more delicate; whilst with mercury and lead they were at least ten times more so. These comparisons were made in aqueous solutions.

In testing urine the value of the electrolytic method is still more evident; for here the colour of the liquid interferes materially with the reliability of the ordinary qualitative tests when only small quantities of the elements referred to are present. This was well instanced in a case of suspected lead poisoning in which the patient had been treated with potassium iodide. A direct test with sulphuretted hydrogen gave no reliable result, even after standing twenty-four hours; whilst the deposit obtained on electrolysis gave a distinct *precipitate* of lead sulphide after being dissolved in acid.

Other applications of the more reliable electrolytic methods of analysis to qualitative work can only offer attraction in special cases, and the data on the subject are to be found in the many electrolytic methods already published. It is by their judicious combination with the ordinary methods of analysis that a saving of time and labour, and, above all, an increased reliability and accuracy is effected.

## THE APPLICATION OF SODIUM PEROXIDE TO WATER ANALYSIS.*

By Dr. S. RIDEAL and H. J. BULT.

Now that sodium peroxide can be obtained commercially its use in analysis seems desirable. W. Hempel (*Zeit. Anorg. Chem.*, iii., 193) has already shown that it is a useful oxidising agent for the detection of chromium and manganese, and that it forms a very convenient reagent for opening up tungsten minerals and for effecting the decomposition of titanic iron ores. Since the commercial sodium peroxide is free from sulphur, it can be used quantitatively for estimating the sulphur in sulphides. It occurred to us that an alkaline oxidising agent of this character, if used as a substitute for alkaline permanganate, in water analysis, might throw some light upon the character of the organic nitrogen in waters. Hitherto either methods for determining the total nitrogen, *e.g.*, Frankland's and Kjeldahl's, or Wanklyn's well-known process, in which only a portion of the nitrogen present in the organic matter is discovered, have been employed. In this latter process very different quantities of ammonia are obtained from the different classes of nitrogenous organic bodies. Only when the nitrogen is present as some simple amido-compound like urea, aspartic acid, or leucine, does this process yield the whole of the nitrogen present.

Preusse and Tiemann (*Berichte*, xii., 1906) have shown, in their review of the various processes for determining organic substances in water, that no reliance can be placed upon this process for estimating the absolute quantity of nitrogen in many substances, and that therefore, when used as a method of water analysis, the quantities of ammonia obtained are only relatively true for waters of the same type. A comparison of the quantities of ammonia evolved from a water when treated with alkaline permanganate and with sodium peroxide, might therefore possibly afford a means of differentiating the nitrogenous constituents. With this purpose in view we have compared, in the ordinary course of analysis, the amounts of ammonia given off under these two treatments. In one case, when using 1 grm. of sodium peroxide per ½ litre of water, the total ammonia evolved was equal to 0·027 part per 100,000, while with alkaline permanganate 0·050 part per 100,000 is obtained. On repeating this experiment, with the same water and under similar conditions, 0·026 part per 100,000 was yielded by the peroxide and 0·048 by the permanganate. The addition of a further quantity of the sodium peroxide and further distilling did not increase the quantity of ammonia produced, and it was therefore evident that the sodium peroxide had failed to break down the organic nitrogenous substances present to the same extent as had the alkaline permanganate. In fact, we have since found it possible to obtain a fresh quantity of ammonia from a water after treatment with sodium peroxide by the addition of the alkaline permanganate.

The following table gives the results obtained in parts per 100,000 with four samples of water.

| | Free $NH_3$. | $NH_3$ from Peroxide. | $NH_3$ from Permanganate after Peroxide. |
|---|---|---|---|
| Water .. .. A. | 0·01 | trace | 0·007 |
| ,, .. .. B. | 0·001 | 0·004 | 0·011 |
| ,, .. .. C. | 0·012 | 0·011 | 0·015 |
| ,, .. .. D. | 0·021 | 0·024 | 0·057 |

| | Free $NH_3$. | $NH_3$ from Permanganate. |
|---|---|---|
| Water .. .. A. | 0·01 | 0·008 |
| ,, .. .. B. | 0·001 | 0·013 |
| ,, .. .. C. | 0·012 | 0·027 |
| ,, .. .. D. | 0·019 | 0·078 |

From these figures it will be seen that the sodium peroxide in no case oxidises the organic matter present to the same extent as does the permanganate. The peroxide seems to liberate a portion of the nitrogen which is included in that set free by the alkaline permanganate, as the total ammonia obtained by the action of the peroxide followed by permanganate is in most cases about equal to that obtained when the water is distilled with alkaline permanganate alone. There appears to be no ratio between the quantities of ammonia evolved by the two reagents, and therefore the nitrogenous organic matter present in waters might be divided into two classes, viz., that which is oxidised by the sodium peroxide and that which resists such treatment. The results obtained by Wanklyn's process, as compared with the total nitrogen present in a water, also show a differentiation in the organic nitrogen substances present in waters; but this knowledge has hitherto not been of any

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* Paper read before the British Association (Section B), Nottingham Meeting, 1893.

value, owing to the complex nature of the problem. Further experiments alone can decide whether the limited oxidation of the nitrogenous matter in water will throw any fresh light on the condition of these organic constituents of water. We have, however, noticed that in some cases a water which has been partially oxidised by the peroxide yields the remainder of its ammonia to the alkaline permanganate with much greater rapidity than when the water has not been so treated. We suggest that the explanation of this phenomenon may be due to the presence in waters of organic nitrogenous substances, which when partially oxidised are then in a condition to be completely broken up by the stronger reagent. This result has been obtained with waters containing fresh sewage; but we hope, by taking solutions containing nitrogenous compounds of known constitution, to confirm this suggestion, and hope thereby to show that in this reagent we have an oxidising agent which will be useful in establishing the constitution of the nitrogen in complex organic substances.

## A NEW METHOD FOR THE RAPID ESTIMATION OF SULPHUR IN STEELS, PIG-IRONS, &c.

By H. A. HOOPER.

The sulphur in steels, pig-irons, &c., is determined, in the following process, by evolving the sulphur in the form of sulphuretted hydrogen by the addition of dilute hydrochloric acid. The sulphuretted hydrogen is absorbed in sodium hydrate solution, and the quantity of sulphur is ascertained by adding a standard solution of lead nitrate until no further precipitate of lead sulphide is formed.

A standard solution of lead nitrate is made by dissolving 3·2265 grms. of pure lead in as small a quantity of nitric acid as possible, and then making this up to 1000 c.c. with distilled water. One c.c. of this solution is equal to 0·0005 grm. S. The following is a description of the process as actually carried out:—Five grms. of steel are dissolved by dilute hydrochloric acid in the apparatus generally used for the determination of sulphur by the evolution process, the absorption-tube being charged with about 10 c.c. of sodium hydrate solution, of about 1·20 sp. gr., and free from sulphide. When the steel is completely dissolved, the contents of the absorption-tube are transferred to a large beaker without any more dilution than is absolutely necessary, and the standard lead nitrate is added in small quantities at a time, agitating the fluid after each addition until it is quite clear) until a drop of the solution gives no further brown colouration. The number of c.c.'s of standard solution used, divided by 100, gives the percentage of sulphur present in the steel.

A single drop of the solution is sufficient to show when the reaction is complete. If a sheet of white paper is placed under the beaker, the final traces of colour are more easily seen.

The delicacy of the above process can be judged from the fact that the sulphur in Swedish pig-irons, &c., can quite easily be determined.

A great advantage of the process is, that the standard solution is quite permanent. The presence of a small quantity of free nitric acid is quite harmless, as it is neutralised by the soda solution, and alkaline nitrates have no immediate action on alkaline sulphides in the cold.

After the substance has been dissolved, the assay can easily be completed within five minutes.

The process has been in use for some time past, and has been proved to be most satisfactory.

Newburn Steel Works, Newcastle-on-Tyne.

### NOTE ON THE

## COMPOSITION OF THE FEN AND MARSH SOILS OF SOUTH LINCOLNSHIRE.

By E. WIGHTMAN BELL, F.C.S.

Very little having been published on this subject it has been suggested to me that the results of analyses of soils of this district would prove of interest. In no case have samples been selected from any supposed superiority, but rather every care has been taken to obtain specimens representative as far as possible of their particular district. Each sample was taken to the depth of six inches, being about the average depth cultivated. A partial analysis of a sample of peaty matter dug up in the fen is appended, being of interest as showing what was the composition of the land before it had been clayed.

The first series of analyses gives the absolute composition of the soil, the solvent used being hydrochloric acid (specific gravity 1·16).

*Peaty Matter from the Fens.*

| | |
|---|---|
| Organic matter and combined water | 67·93 |
| Silica and insoluble matter | 18·53 |
| Ferric oxide and alumina | 8·51 |
| Lime | 2·23 |
| Phosphoric acid | 0·25 |
| Sulphuric acid | 1·04 |
| Alkaline salts, &c. | 1·51 |
| | 100·00 |

*Fen Soil.*—No. 1.

| | |
|---|---|
| Organic matter and combined water | 26·47 |
| Silica and insoluble matter | 55·88 |
| Ferric oxide | 11·56 |
| Alumina | 1·18 |
| Manganous oxide | 0·13 |
| Lime | 1·44 |
| Magnesia | 0·28 |
| Potash | 0·42 |
| Phosphoric acid | 0·26 |
| Sulphuric acid | 0·76 |
| Carbonic acid, soda, &c. | 1·62 |
| | 100·00 |

*Fen Soil.*—No. 2.

| | |
|---|---|
| Organic matter and combined water | 22·78 |
| Silica and insoluble matter | 59·53 |
| Ferric oxide | 8·66 |
| Alumina | 4·48 |
| Manganous oxide | 0·05 |
| Lime | 1·50 |
| Magnesia | 0·34 |
| Potash | 0·43 |
| Phosphoric acid | 0·21 |
| Sulphuric acid | 0·41 |
| Carbonic acid, soda, &c. | 1·61 |
| | 100·00 |

*Fen Soil.*—No. 3.

| | |
|---|---|
| Organic matter and combined water | 16·13 |
| Silica and insoluble matter | 75·34 |
| Ferric oxide | 3·45 |
| Alumina | 1·85 |
| Manganous oxide | 0·02 |
| Lime | 1·02 |
| Magnesia | 0·42 |
| Potash | 0·28 |
| Phosphoric acid | 0·16 |
| Sulphuric acid | 0·32 |
| Carbonic acid, soda, &c. | 1·01 |
| | 100·00 |

*Marsh Soil.*—No. 1.

| | |
|---|---|
| Organic matter and combined water | 4·63 |
| Silica and insoluble matter | 85·49 |
| Ferric oxide | 4·95 |
| Alumina | 0·84 |
| Manganous oxide | 0·08 |
| Lime | 2·16 |
| Magnesia | 0·40 |
| Potash | 0·16 |
| Phosphoric acid | 0·16 |
| Sulphuric acid | 0·15 |
| Carbonic acid, soda, &c. | 0·98 |
| | 100·00 |

*Marsh Soil.*—No. 2.

| | |
|---|---|
| Organic matter and combined water | 4·54 |
| Silica and insoluble matter | 84·03 |
| Ferric oxide | 4·22 |
| Alumina | 2·70 |
| Manganous oxide | 0·02 |
| Lime | 2·12 |
| Magnesia | 0·28 |
| Potash | 0·20 |
| Phosphoric acid | 0·21 |
| Sulphuric acid | 0·30 |
| Carbonic acid, soda, &c. | 1·38 |
| | 100·00 |

A second series of analyses was then made with a view of showing the amount of plant food in a readily available condition. In this case the solvent used was acetic acid (specific gravity 1·04). The results are percentages calculated on the dry soil.

*Fen Soil.*—No. 1.

| | |
|---|---|
| Ferric oxide | 1·326 |
| Alumina | 0·579 |
| Lime | 0·944 |
| Magnesia | 0·231 |
| Potash | 0·112 |
| Phosphoric acid | 0·015 |

*Fen Soil.*—No. 2.

| | |
|---|---|
| Ferric oxide | 0·481 |
| Alumina | 0·781 |
| Lime | 0·824 |
| Magnesia | 0·165 |
| Potash | 0·242 |
| Phosphoric acid | 0·113 |

*Fen Soil.*—No. 3.

| | |
|---|---|
| Ferric oxide | 0·298 |
| Alumina | 0·873 |
| Lime | 0·843 |
| Magnesia | 0·089 |
| Potash | 0·036 |
| Phosphoric acid | 0·022 |

*Marsh Soil.*—No. 1.

| | |
|---|---|
| Ferric oxide | 0·309 |
| Alumina | 0·248 |
| Lime | 1·823 |
| Magnesia | 0·290 |
| Potash | 0·034 |
| Phosphoric acid | 0·040 |

*Marsh Soil.*—No. 2.

| | |
|---|---|
| Ferric oxide | 0·199 |
| Alumina | 0·333 |
| Lime | 1·001 |
| Magnesia | 0·155 |
| Potash | 0·121 |
| Phosphoric acid | 0·013 |

High Bridge, Spalding.

## AN INTERNATIONAL INDEX TO CHEMICAL LITERATURE.

### Opening Address to the Section of Bibliography, Congress on Chemistry, held at Chicago, August 21st—26th, 1893.

By HENRY CARRINGTON BOLTON,
Chairman of the Section.

During one of my bibliographical tours in Europe, an eminent librarian of a German university remarked:—"You Americans are doing more and better work in bibliography than all the nations of Europe taken together." And this he said not in flattery, but as the expression of an earnest conviction. Later I expressed surprise that Germans, with such splendid collections of books and other advantages, should leave it to Americans to cross the Atlantic and wrest from Europe materials for general and special bibliographies. To this he promptly replied: "Ach, mein Freund, das Geld fehlt."

I shall not attempt to demonstrate the accuracy of the gentleman's statements, as it would involve comparisons, and these are said to be odious. A basis for his enthusiasm is, however, found in such monumental works as "Pool's Index," "Fletcher's Index," Billing's "Index Catalogue of the Medical Library of the Surgeon General's Office," the "Index-Medicus" (edited by Dr. Robert Fletcher), the Catalogue of the Boston Athenæum, as well as the bibliographies of science published by the Smithsonian Institution, by the U.S. Department of Agriculture, and in independent journals. Many other notable works will suggest themselves to the chemists present, who will understand that this is only a passing reference.

The production of special and general bibliographies in the United States goes forward with the multiplication of public and endowed libraries, now increasing in number and value with gratifying rapidity throughout the land. Some of these are publishing bibliographies of specific subjects in addition to their library catalogues; in this direction Harvard University takes the lead.

Unfortunately, much good work done by Institutions does not get beyond the M.S. stage, as, for example, the subject-index in preparation at the Scientific Library of the United States Patent Office, and the chemical bibliographies compiled by the Students of the University of Michigan as appendages to theses in science.

There are at least three organisations in the United States which promote the preparation of bibliographies; these are the American Library Association, the Committee on the Bibliography of Geology appointed at the International Congress of Geologists, and the Committee on Indexing Chemical Literature, of the American Association for the Advancement of Science. The work of the American Library Association is familiar to everyone; through the journal it reaches all librarians and bibliographers in sympathy with its enterprises. Its scope is, however, almost entirely literary, and science finds little place in its admirable plans.

The Secretary of the Committee on the Bibliography of Geology appointed at the International Congress of Geologists, held September 1st, 1891, at Washington, has issued a circular, dated November 20, 1891, which sets forth its plans for work. These comprise the preparation of (1) a list of the geological bibliographies already in existence; (2) new bibliographies of special topics; and (3) the periodic registration of the current bibliography of geology. Their work has been so recently begun that no great results can as yet be expected.

The work of the Committee on Indexing Chemical Literature, of the American Association for the Advancement of Science, now in the eleventh year of its existence, is familiar to most persons present. This Committee has endeavoured to direct attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little systematic work has been undertaken, duplication of labour has been prevented and independent efforts have accomplished much. Thus a collection of special bibliographies has been gradually forming, which now number more than fifty; the list was printed in the tenth annual report of the Committee, published in the *Proceedings of the A. A. A. S.* for 1892, as well as in the CHEMICAL NEWS (London). While the Committee feels that their labours have not been in vain, the proportion of the completed bibliographies to the number of authors publishing chemical papers is still unhappily small, and the average of five bibliographies per annum is rather lower than expected. The Committee expresses the hope that the number will grow much faster in the future.

In England, the British Association for the Advancement of Science has done something towards fostering the object under consideration by appointing Committees on Indexing Solutions and other topics, but their work progresses slowly.

The Chemical Societies of Berlin, Paris, and London give to their members and subscribers laboriously prepared abstracts of papers published in countries other than their own. For persons whose linguistic attainments are limited to their mother tongue these abstracts are undoubtedly useful, perhaps invaluable; but it rarely happens that they can be entirely relied upon for the details needed by chemists practically interested, and the originals must eventually be consulted. It has seemed to me that if the same amount of energy expended by abstractors of the Societies named could be exerted in indexing, greater practical results would be obtained, and at far greater economy of space. Moreover, these Societies generally confine their abstracts to publications issued in other countries than their own, and consequently a large amount of good material published at home in Government reports, Transactions of learned Societies, and periodicals devoted to general science escapes the eyes of all except a few industrious readers.

It has further occurred to me that the chemical societies of Germany, France, Italy, Russia, England, and the United States, instead of filling their official organs with abstracts of papers foreign to each, might well devote their energy to indexing the wealth of material produced each in its own nation.

And this brings me to the statement of a plan which I have the honour to propose to this Congress, for a Co-operative International Index.

I suggest that this Congress, in which are representatives of the six leading Chemical Societies of the world, recommend to these Societies the preparation of an annual index to current chemical literature, each Society to care for the productions of the country in which it is situated. These annual indexes to chemical literature could be published in the journals (Berichte, Bulletin, Journal, &c.) of the respective Societies; which fortunately for our purpose are all in octavo form; and when all the indexes are issued for a given year, they could be bound together for convenience. The bibliographies would, of course, be compiled on the same or similar plans; this uniformity being secured by conference between the Index Committees of the several Societies. This plan would necessitate the consultation of six alphabets at least in each annual volume, but this inconvenience would be counterbalanced by the greater accuracy and fulness attained by the sub-division of labour proposed.

What reception this plan may receive by the severa societies is uncertain; but I believe that no more important work can be undertaken by the American Chemical Society. This newly re-organised association now numbers over seven hundred members, and is a truly national society; the Journal could not present to its members and subscribers a more welcome contribution than a subject-index to the publications of American chemists. This might be done half-yearly—or, better, quarterly—and should embrace the widest range of pure and applied chemistry. Perhaps the American Chemical Society will lead in this enterprise, and then the older and more conservative societies of Europe might follow. One stimulus that would eventually influence them is national pride.

So far, this plan relates only to current literature, and some provision must be made for indexing the enormous accumulation of material already in print. Probably there is no better way to attack this problem than to prepare a subject-index to the chemistry contained in the catalogue of scientific papers published under the auspices of the Royal Society. This monumental work loses much of its value owing to the lack of a subject-index, and it is deeply to be regretted that there is no prospect of one being compiled, if at least one may judge from the correspondence on this subject printed in the pages of *Nature*.

And here allow me to place on record a fact bearing on the question. A few years ago a member of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, already known to the scientific world by his labours in bibliography, decided to undertake the preparation of a subject-index to the chemistry and physics in the eight quarto volumes of the work named; but before doing so wrote a courteous letter to the secretary of the Royal Society announcing his scheme. In that letter the gentleman explained that he planned to compile the subject-index and to print it entirely without expense or liability on the part of the Royal Society. After a long lapse of time the gentleman received a note from the secretary of the Royal Society stating that the matter had been laid before the Council, and they had refused permission to have such an index prepared! Thus rebuffed, my friend abandoned his scheme and turned his attention to another task.

In spite of this attitude of the Council of the Royal Society, I believe a regularly constituted Committee of chemists could secure permission, if indeed any be necessary.

Details of methods to be pursued cannot here be considered; they could be formulated by a Committee.

A general bibliography of chemistry has been recently attempted by the writer of this communication; the results form a volume of over twelve hundred pages just issued by the Smithsonian Institution as No. 850 of the series entitled Miscellaneous Collections. This "Select Bibliography of Chemistry" (1492—1892) embraces about twelve thousand titles in twenty-four languages, yet makes no claim to completeness. It is, moreover, a bibliography, not an index.

In conclusion, I have the honour to propose the appointment of an International Committee on Chemical Bibliography, to consist of one member from each country represented in this Congress. That this Committee have unlimited power to add to its number, provided, however, that no country have more than two representatives. That this Committee, through the European and American Chemical Societies, report a scheme for an International Co-operative Index to Chemical Literature.

University Club, New York City,
August, 1893.

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This paper was referred to a Committee, who then reported as follows:—

TO THE CONGRESS ON CHEMISTRY:

Your Committee, having considered the suggestions of Dr. Bolton, recommend that a communication be addressed from this Congress to the national chemical societies of England, France, Germany, Italy, Russia, and America, reporting the following action by this Congress:—

"Whereas, Some activity has been shown of late years in the compilation of bibliographies of various subjects, but without the uniformity and system which are desirable.

*Resolved*, That we recommend the annual publication of classified bibliographies by the chemical societies of

England, France, Germany, Italy, Russia, and America, for these several countries.

*Resolved*, That we recommend each of these societies to appoint one representative upon an International Committee to confer together and report to the several societies a scheme for an International Co-operative Index to Chemical Literature."

Respectfully submitted,
(Signed) Edward Hart,
Robt. B. Warder, } Committee.
Wm. L. Dudley.

## ON ERBIA.*

By GERHARD KRÜSS.

Continued from p. 178).

In order to render this result certain and to raise the objection that the true erbia might perhaps have not been brought, by an unsuitable arrangement of the above experiments, into the materials which we called Nos. 1 to 7,† both the more feebly basic and the more strongly basic oxides were examined for the presence of Er=166. The elaboration of the stronger bases coincides with an investigation of holmia which is also already concluded. According to those experiments, no $Er_2O_3$ with a constant Er=about 166 could be isolated from the holmia earth. The examination of the more feebly basic earths which approached nearest to the erbia earth gave the following results:—

As the material, there were used fractions 1 and 2 of Series 10. They stand on the side of weaker basicity nearest to the erbia material No. 6, which is identical with fraction 3 of Series 10.

To the fractions 1 (172·4) and 2 (172·9) of Series 10 there were further added as a precaution the feeblest bases of the thulium material fraction 1 (171·6), Series 8; this also was a material in which a little erbia might be present.

From these three united fractions precipitations of solutions were alternately effected with aniline hydrochlorate, so that we obtained—

*Series* 15.

Weaker bases ←——.
Aniline precipitates.

| 1 | 2 | 3 | Middle |
|---|---|---|---|
| 173·4 | — | 173·0 | 172·0 |

——→ Stronger bases.
Aniline solutions.

| 4 | 3 | 2 | 1 |
|---|---|---|---|
| 167·5 | 168·8 | 166·9 | 165·3 |

We have here the same phenomenon as in working up the above-mentioned erbia materials in general; the ytterbia earth can be relatively easily and well separated from the erbia earth; further, there remains in the fractions of Series 15 obtained by the aniline solutions Nos. 4, 3, and 2 the $\overset{\text{III}}{R}$ for the earth approximately constant =167 to 168. The last three fractions (167·5, 168·8, 166·9) were united, and were now resolved by aniline hydrochlorate into three fractions and a residue—the precipitate remaining from the third solution.

Stronger bases ←——. ——→ Weaker bases.

|  | 1 | 2 | 3 | 4 | Remnant. |
|---|---|---|---|---|---|
| Series 16. | 161·8 | 164·5 | 168·9 |  | 171 |

There existed, therefore, no unitary erbia earth in the earths which were adjacent to the erbia materials Nos. 6 to 8. The last-mentioned experiments even confirm the result obtained in Series 14, that the erbia is relatively easily decomposed by aniline hydrochlorate when certain quantities of earths having values $\overset{\text{III}}{R} > 168$ and $< 166$ are eliminated from the erbium material.

The above experiments were executed with erbiferous earths derived from 5 kilos. of gadolinite. But as the object was to obtain pure $Er_2O_3$, and not to prepare large quantities, the erbia material No. 6 represented a quantity of only about 2 grms. of earth. I had therefore great pleasure in obtaining from Herr L. F. Nilson considerable quantities of erbia earths, which served to repeat the above experiments and confirm or modify their results. I obtained from L. F. Nilson—

1. 98 grms. erbia earth, according to Nilson about =165; my own determination gave $\overset{\text{III}}{R}=164·7$.
2. 24 grms. erbia earth, according to Nilson $\overset{\text{III}}{R}=164$ to 165; my own determination =165·3.
3. 22·5 grms. erbia earth, according to Nilson $\overset{\text{III}}{R}$ probably greater than 165; my own determination $\overset{\text{III}}{R}=166·9$.

The earths Nos. 1 and 2 were obtained from the same material from which L. F. Nilson, in 1879 and 1880, obtained pure ytterbia and scandia. Both oxides had an equally fine rose colour, and the solution of the chlorides gave an absorption-spectrum with lines at $\lambda = 669·0^1$—$654·7^3$; Erα, $640·0^1$; Xα, $558·6^1$; Smβ, $543·0^1$; Xβ, $539·9^2$ (?)—$523·1^3$; Erβ, $488·8^1$ (?)—$485·5^2$; Xδ, $474·5^3$; Xε, $428·5^2$ Xη.

Nilson's third erbiferous earth was obtained from materials of a different origin, and had a similar colour to the preparations 1 and 2, but with a lilac cast. The lilac-rose coloured solution of chlorides yielded an absorption-spectrum like the two other preparations, but besides the above-named lines, it displayed bands at $\lambda = 542·6^3$; Xβ, $539·9^1$ (?); λ 428·8 Xη was absent in the spectrum of this substance. (The exponents placed after the wave-lengths of the bands are to show approximately the intensity, increasing with magnitude of the exponents).

(To be continued.)

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 181).

*Hydrocarbon*, No. 2152.—Luminous in an electric discharge tube closed with quartz; pressure = a mercurial column of 3 m.m. Exposure, twenty-five minutes. Ten new bands, decreasing very regularly in efficacy and intensity with its wave-lengths; the last band appears as a faint shadow between the two components of line No. 32.

Another proof with the same tube (No. 2153) gave, with a double width of slit (0·080 m.m.) and 2½ hours' exposure, the entire spectrum stronger, but still very clear, and traces of two new bands beyond 185·2.

All these spectra, I must add, like the spectrum of aluminium, have acted much more feebly in their more refrangible half than in the rest of the ultra-violet. As

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* *Zeitschrift fur Anorganische Chemie.*

† It is certain that these materials, according to their spectrum and to the determination of their equivalents, must contain Er=166 to 168 if it exists.

* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

far as the region of the most refrangible cadmium rays they consist of a deep black band, interrupted at most by single, solarised lines, which stand clear as glass. In the other part, even on the most prolonged exposure, I have never seen such a confluence of the lines, still less solarisation.

As results from the above conspectus, it is common to all the proofs that they develope a greater or less abundance of rays in the most refrangible part of the spectrum, where hitherto only the few lines of aluminium had been known; that most of them overstep the previous limit of the ultra-violet; and, further, that they finish with almost the same wave-length.

I next hoped to attain more by prolonged exposure, and by sparks of still greater energy. I increased the number of the immersed elements, as also the number of the Leyden jars; substituted for the inductorium an influence machine, which, in combination with the Riess battery, gave very energetic sparks; altered the composition of the coating of my plates, increasing the proportion of iodine, so as to heighten the sensibility; sensitised my plates by fuming with ammonia;—in short, I sought, by all means to penetrate further into the ultra-violet. But what I gained was scarcely worth mentioning. In some spectra there was a slight increase in length, but beyond the wave-length, 182 $\mu\mu$, not the trace of a line.

It is a phenomenon universally observed in spectral photography that the photography of greatly enfeebled rays involves extraordinary difficulties, and that exposure, however prolonged, does not yield clear images. I have regularly encountered this evil at the limit of the transparency of the material of the prism: in heavy flint-glass at the very beginning of the ultra-violet, in light flint-glass near the Frauenhofer line O, and in crown-glass near R. It is the same at the limit of the transparency of the air, the position of which, as appears sufficiently from the foregoing, depends on the thickness of the stratum of air. That the result, at any rate to a small extent, depends also on the degree of sensitiveness of the photographic plate is proved by the fact that I obtained the spectrum of the June sun (from my laboratory, about 120 metres above the level of the Baltic), beyond the Frauenhofer line U, upon Zettnow's plates, whilst the same line could not be obtained upon other plates at the same time. Still the photographic result in the most refrangible ultra-violet would have fallen out far better if the light which originates on the refractive phases and in the interior of the prisms and lenses had not regularly illuminated the visual field so strongly that on prolonged exposure the whole plate is coloured more strongly than the spectrum itself. We might indeed, as I observed in 1888, with the photographic spectrum apparatus of Simony, considerably reduce the diffused light by shortening the slit length to a minimum (0·2 m.m.); but even here, on prolonged exposure, it overpowered the delicate impression of the most refrangible rays to total invisibility.

The contraction of the length of the slit was the last expedient which had opened up the prospect of better results as long as I was limited to the apparatus employed.

If we collate the results of the proofs obtained with a short focal distance, it follows:—

1. That on sufficient diminution of the absorption of the rays by the air, nothing further stands in the way of the exploration of the spectral region between the wave-lengths 200 $\mu\mu$ and 185 $\mu\mu$, and that the existing means of observation are fully sufficient.

2. That nearly all the electrodes tried emit photographically effective light beyond the limit of the ultra-violet, as hitherto observed.

The appearance of rays beyond the wave-length 185·2 $\mu\mu$ gave an altered direction to my work; instead of the known spectrum it now referred to the opening up of the unknown luminous region between the wave-lengths 185·2 $\mu\mu$ and zero.

The following portion of my report treats of the means for this purpose and the present position of the solution of this problem.

(To be continued.)

ON THE

# ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 183).

## Salicylic Acid ($C_6H_4OH.CO_2H$).

A solution was prepared containing 2 grms. salicylic acid and 3 grms. caustic soda in 150 c.c. of water. 15 c.c. of this solution was made up to 300 c.c. with water, the whole heated to 60° C., and the iodine solution run in to large excess. This process was repeated until a sufficient quantity of the product was obtained. The precipitate was of a violet-red colour, and of similar appearance to that obtained with simple phenol.

The precipitate, after drying, was boiled with alcohol, but the soluble portion being so slight was neglected. The remainder was treated with warm ether, but here again only a small portion dissolved out. The remainder was boiled with chloroform, which dissolved out a rather larger quantity. The remainder was then collected and dried, when it appeared as a pinkish red pulverulent substance, which did not melt, but decomposed at a high temperature (about 370° C.). It was cautiously heated on a mercury bath at a temperature of about 350° C. until it had lost its red colour, that is, until the "encluded" iodine had been dissipated. The product, which was of a dirty white colour, was practically insoluble in carbon disulphide.

Total iodine of this product:—
Quantity taken =0·1636 grm.
Silver iodide found=0·2120 „ =70·03 p.c. iodine.

Combustion of same:—
Quantity taken =0·1334 grm.
Water found =0·0117 „ = 0·97 p.c. hydrogen.
Carbon dioxide found =0·1009 „ =20·63 „ carbon.
By difference .. .. = 8·37 „ oxygen.

Those results may be formularised thus, $C_{12}H_5I_4O_4$.

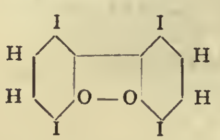
Another batch was prepared from salicylic acid with a total dilution, prior to the addition of iodine, equal to about a half that used in the last case, under otherwise similar conditions.

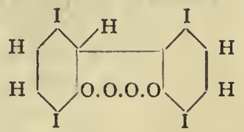
The precipitate, which was of similar appearance, was treated with the various solvents in the same order as before. The quantities dissolved out by alcohol and ether were little more than traces, but the quantity taken out by chloroform was rather greater than in the previous case. The remainder of the precipitate from the chloroform treatment was treated with carbon disulphide, in which it almost wholly dissolved, forming a fine violet-red coloured solution. The solution was filtered and the solvent evaporated off. The residue was quite similar in appearance and properties to that similarly obtained from the simple phenol precipitate. It was powdered and heated for about two days at a temperature of about 345° C., at the end of which time it had almost entirely lost its red colour. It was then taken for analyses.

Total iodine:—
Quantity taken =0·1664 grm.
Silver iodide found=0·2274 „ =73·83 p.c. iodine.

Combustion of same:—
Quantity taken = 0·1086 grm.
Water found = 0·0078 ,, = 0·79 p.c. hydrogen.
Carbon dioxide found = 0·0852 ,, = 21·39 ,, carbon.
By difference .. .. = 3·99 ,, oxygen.

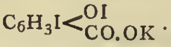
Those results may be represented by the formula $C_{12}H_4I_4O_2$. This and the substance previously examined being represented respectively, thus:—





It is apparent, therefore, that the products derived from salicylic acid are essentially the same as those from simple phenol as the result of this iodine reaction, the group COOH being wholly removed, as might have been premised.

The total iodine percentages for the precipitate obtained with salicylic acid, reported by M. and V., are 61·01, 59·73, and 60·56. It is evident from those results that they had obtained a precipitate containing on the average only one atom of iodine in each benzene nucleus (granting that the precipitate was otherwise practically the same as that examined by me). This is somewhat remarkable when compared with the case of phenol. They consider it to be the potassium salt of the iodine derivative of salicylic acid. When they digested it with acid it let fall a red powder, and when boiled with caustic potash solution it retained its iodine as the di-iodo-phenol-iodide, and passed in great part into solution. When they acidified this there fell out a white crystalline precipitate which contained iodine and melted about 165° C.; this they thought was probably the di-iodosalicylic acid already known. They represented the original precipitate thus—



$$C_6H_3I<^{OI}_{CO.OK}\cdot$$

Taken alongside the results found by me, it is difficult to reconcile some of those statements made by M. and V., but without fuller evidence of the essential identity of the two precipitates it would be useless to criticise them. At all events, however, it would be exceedingly unlikely that they had obtained the potassium salt of di-iodo-salicylic acid as a precipitate. Further, since they state the colour of the precipitate as being dark red, this is conclusive evidence in itself that the precipitate contained a relatively large proportion of the oxidised products, which colour is mainly due to "encluded" iodine, and such "encluded" iodine is peculiar to such products, confining those remarks to the substituted phenols and their allies.

The principal incongruities may very probably be explained away by assuming that M. and V. had only used a meagre excess of iodine in preparing the precipitate.

(To be continued).

**Examination of Lanoline.**—The method given by Helbing and Passmore (*Zeit. Anal. Chemie*, xxxii., 115) has been repeatedly examined and pronounced useless. W. Graff (*Pharm. Zeitung*) finds lanoline more or less attacked by aqueous potassa-lye. On working according to Helbing and Passmore with alcoholic potassa moderately constant results may be obtained; but the lanoline is not entirely split up at the temperature of the water-bath in two hours, so that the constant of saponification given by the above-named authors (8·536) is too low. According to Kremel 9 parts KOH are required for the saponification of anhydrous lanoline. If a hydrocarbon (vaseline) is present along with glycerin fat, the method of saponification gives utterly worthless results.

## NOTICES OF BOOKS.

*Methods of Practical Hygiene.* By Prof. K. B. Lehmann, Wurzburg. Translated by W. Crookes, F.R.S. In Two Volumes, with numerous Illustrations. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1893. 8vo., pp. 433 and 468.

We have here a very comprehensive work on the methods employed in sanitary inquiries. The author has more especially kept in view the requirements of the physician, whether in private practice or as medical officer of health. But much of the instructions here conveyed will be valuable to scientific chemists, pharmaceutists, and lawyers.

The author's point of view is throughout moderate and judicious. He eschews sensational and alarmist statements, and suggests no sweeping measures. Where our present knowledge is insufficient to warrant a decided opinion, he admits the difficulty. Sanitary experts who adopt his principles, which are substantially those of the late Dr. Angus Smith, will never bring Science into disrepute by contradicting each other in Court.

The present version is founded on a copy revised, corrected, and extended by the author according to the most recent investigations. The text, as may be found on a careful examination, has been literally followed. In the many cases where the differences of laws and customs in Britain and in Germany rendered it necessary, and where the views of the editor slightly differed from those of the author, footnotes have been added. The comparison of German laws and decisions on the pollution of drinking-waters, and on the sophistication of food, with those existing or proposed in Britain, should render this work especially interesting to the legal profession and to legislators.

The author begins with general methods, chemico-physical and bacteriological, followed by general indications on hygienic toxicological inquiries. Here dietetic experiments on animals are recommended as necessary, which, as the editor does not omit to inform his readers, are practically speaking illegal in Britain.

In the "special part" we have instructions for special investigations, *i. e.*, the examination of air in its physical relations and its chemical composition, and as to the quantity of corpuscular matter. This section, like most other parts of the work, is plentifully and judiciously illustrated.

The examination of soils is next entered upon, to decide whether any plots of land are suitable for human habitations, for cemeteries, or for irrigation fields. Especial attention is given to the bacteriological examination as throwing light on the occurrence of malaria. We note the interesting remark that "the Bavarian moor-lands which suffer from malaria have a striking immunity from cholera."

We agree with the editor that Prof. Lehmann seems disposed to under-estimate the dangers of grave-yards. We cannot find that he refers at all to cremation.

Water meets with elaborate treatment. Its examination—chemical, microscopic, and bacteriological—is very fully described. There are also chapters on river-pollution, on sewage, and on filters. The suitability of a water for technical purposes is merely sketched.

Next we arrive at the general methods for the examination of foods. The "chemical preservatives" now often added to foods very rightly find here little favour. The reasons against the use of such additions are given in a manner which must commend itself to every person able and willing to judge.

Following on the general examination of foods come the special sections on the scrutiny of meat, including the detection of animal and vegetable parasites, poisons, and incipient decomposition. Preserved meats are similarly scrutinised.

Next follows milk. We are glad to note that the lactoscope, the lactometer, and the cremometer meet here with little countenance. For the determination of fat the Adams and the Soxhlet methods are recommended. The microbia commonly found in milk—some of them pathogenic—are duly noticed. Of these the most important is the bacillus of tubercle. The "cow-house test" is described in full.

Butter and cheese, with their alleged adulterations, follow next, though some reported sophisticants are considered as not proven.

Under flour and bread come instructions for detecting diseased grains of cereals and the seeds of weeds, such as corn cockle and—above all—ergot. The last-mentioned product contains *three* poisons,—the paralysing ergotic acid, sphacelic acid (which occasions gangrene), and the highly poisonous cornutine. Concerning the physiological action of the seeds found accompanying grain, the statement of observers are often discordant. "Panin-meal" consists of dirty crusts collected in hotels, &c., slightly roasted, ground up and mixed with flour, or used to thicken soups. We have not yet acclimatised this unpleasant fraud in Britain.

In preserved fruits and vegetables the addition of copper is shown to be undesirable, but less dangerous than it is commonly supposed.

Our knowledge of fungi is insufficient. Their value as foods is much lower than a mere determination of their nitrogen might seem to prove, since much of this nitrogen is present in the form of non-assimilable amido-compounds.

A section is devoted to sugar, honey, and Fahlberg's saccharine, which the author pronounces non-poisonous.

Coffee seems to have been selected as the especial notion of fraudulent ingenuity — witness the spurious coffee-beans made on the Continent. Here very drastic legislation is urgently needed.

As regards cocoa and chocolate, the Association of German Chocolate-makers have done much to discourage fraud. Any addition of starch must be shown on the packages. Spices seem to be grossly falsified abroad. Factories exist in Austria for preparing so-called matta-powder—an abominable mixture with sometimes lead chromate, and which is used for sophisticating pepper, cassia, pimento, &c.

The various fermented and distilled liquors are discussed at great length. The attempt to counteract the "plastering" fraud by the addition of barium chloride may lead to serious consequences.

Clothing and its materials are next considered from a hygienic point of view, and with especial reference to different climates.

An important section is taken up with the sanitary examination and decision on dwelling-houses. Here we have notice of cellar-dwellings, roof-dwellings, walls, windows, artificial lighting, coal gas, petroleum, the electric light, ventilation, heating, water-supply, house-sewage, and closets. Next we have the hygienic examination of household appliances by which poisons or infections may be introduced. Disinfection is finally judiciously considered.

To all the more important sections there are appended very full references to the literature of the subject.

Prof. Lehmann's book must form an invaluable work of reference for medical officers of health, public analysts, town clerks, and in general to all medical men, chemists, and engineers, who ever have to concern themselves with sanitary questions.

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*Agricultural Journal.* Published by the Department of Agriculture of the Cape Colony. Vol. vi., Nos. 15 and 16.

In an article borrowed from the *Melbourne Weekly Times* we find the following sensible caution :—"The secret of successful irrigation is only to apply the water as often as in your judgment the plants or trees seem to require moisture." How different is this from the practice of our sewage irrigationists.

The prickly pear, invaluable for fences, but now becoming—both at the Cape and in Australia—a very troublesome weed, is now being combated with sodium arsenite! We fear that without due care and judgment the remedy may become as bad as the disease.

The banana crop is now threatened by the "banana blight," but spraying with "Bordeaux broth" (copper and lime) seems to be an effectual remedy.

The fruit trade seems to have a great future before it. The Union and Castle lines of steamers enter thoroughly into the spirit of the trade.

The name wire-worm, generally applied in the old country to the larvæ of certain Elaters so destructive to root crops, is now extended to *Strongylus contortus*, recently known as *Filoria hamata*, which is as dangerous to sheep as the other wire worm is to vegetation.

The farmers and gardeners are much exercised by the inroads of the spring hare (*Pedetes capensis*), a burrowing species.

We hope that the *Agricultural Journal* may be duly appreciated as it undoubtedly deserves.

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## CORRESPONDENCE.

### PREPARATION OF HYDROGEN.

*To the Editor of the Chemical News.*

Sir,—Referring to Mr. John Ball's letter on the "Preparation of Hydrogen," which appeared in the Chemical News, vol. lxviii., p. 184, your readers may be interested in knowing that I used a solution of cobalt nitrate for the rapid evolution of hydrogen for laboratory and lecture room use when I was lecture-assistant to the late Prof. W. Dittmar, of the Anderson's College, in 1876, not considering at the time it being anything new.—I am, &c.,

G. C. MacDonald.

4, Roslea Terrace, Kelvinside, Glasgow,
October 14, 1893.

### BARIUM SULPHATE IN SANDSTONE.

*To the Editor of the Chemical News.*

Sir,—In reference to the above it may be of interest to Prof. Clowes to know that barium sulphate occurs in the millstone grit at Houghton's Quarry, near Skelmersdale, in Lancashire. The rock is a fine-grained white sandstone, the cementing material being largely carbonates of lime and magnesia (dolomite in joints), and containing also a little barium sulphate, which may be found compact in crevices. The actual amount in the rock was not determined quantitatively.—I am, &c.,

H. T. Mannington.

Flint, North Wales,
October 16, 1893.

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Medal.—Dr. A. B. Griffiths has been awarded a bronze medal by the Committee of the Gardening and Forestry Exhibition (Earl's Court) for his books on Manures and "in testimony of the appreciation in which the Committee hold his valuable aid in contributing to the Exhibition."

Distinction between Natural Butter and Margarine.—F. Gantter.—The author concludes that pure butter fat, with the sulphuric acid test, must take merely a straw or reddish yellow colour, but not a deep brown. Its iodine number must not exceed 16.—*Zeit. Anal. Chemie*, xxxiii., Part 4.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

**Note.**—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 14, October 2, 1893.

**Fixation of Iodine by Starch.**—G. Rouvier.—The author has obtained the following results:—The weights of starch remaining the same, as well as the other conditions of the experiment, if we increase the percentage of iodine employed the quantity of iodine fixed increases at first progressively. If we employ iodine in sufficient quantity we obtain a compound the percentage of iodine in which differs very little from 19·6, corresponding to the formula $(C_6H_{10}O_5)_{16}I_5$. He has never obtained a larger proportion. The weights of iodine and of starch remaining the same, as well as the other conditions of the experiment, if the volume of the mixture continually increases, the quantity of iodine fixed decreases, though on condition that we do not use a quantity of iodine much greater than that necessary for obtaining the proportion of 19·6 per cent.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 3.

**Examination of Paper.**—M. Stockmeier (Eleventh Congress of Bavaria Technical Chemists).—The author extends previous researches on the injurious action of certain papers on leaf-metals. He tests the papers on Kämmerer's principle for their behaviour with leaf-silver by stratifying five samples of the papers to be examined with leaf-silver, folding the packets together, and letting them lie for twenty hours at 50° between watch-glasses in a place free from acids and hydrogen sulphide. If the metal is visibly attacked or discoloured, the paper is unfit for wrapping objects of metal. For the detection of sulphurous acid (which renders papers unfit for packing steel wares) the author distils 50 grms. of the sample in a current of steam in an apparatus filled with carbonic acid, and receives the distillate in iodised potassium iodide. Papers containing chlorides or alums are not suitable for packing articles of steel. Sulphurous acid or sulphites may be detected in papers by conversion into hydrogen sulphide by means of zinc and phosphoric acid. The absence of substances which give off hydrogen sulphide with acids must first be ascertained. For the detection of free sulphuric acid the author (in concert with Wurster) finds Congo paper too sensitive. He extracts 10 grms. of the paper in question with alcohol in an Erlenmeyer flask, concentrates the extract to a minimum with the addition of water, and tests the drop of liquid thus obtained with methyl violet. A simultaneous blank experiment must give a negative result.

**Analysis of Iron.**—This and the following paper are too voluminous to be inserted in full.

**Determination of Phosphorus in Steel and Iron.**—A. von Reis (*Stahl und Eisen* and *Zeit. f. Angew. Chem.*).

**Examination of Salipyrine.**—J. Altschul (*Pharm Central Halle*).—The author dissolves 3·26 grms. of the specimen in a little alcohol diluted with half its volume of water, heating on the water-bath, and titrates with normal alkali until redness appears, using phenolphthalein as indicator. The tenths of a c.c. consumed give at once the percentage of antipyrine salicylate in the sample. Antipyrine has no action upon phenolphthalein.

**Determination of Alkaloids.**—Ledden Hulsebosch.

**Determination of Resinous Matter in Jalap.**—F. H. Alcock.—From the *Pharm. Journ.*, 1892, 1154, p. 107.

**The Atomic Weight of Nickel.**—G. Krüss and F. W. Schmidt.—The authors conclude that purified nickel of the atomic weight 58·6 still contains small quantities of a substance of a high atomic weight.

## MISCELLANEOUS.

**The Glasgow and West of Scotland Technical College.**—The secretary of this establishment has kindly sent us a syllabus of the lectures to be delivered before its members during the ensuing winter session. Most of the subjects selected seem to belong rather to mechanical engineering than to chemistry or its applications. We may, however, call attention in particular to the lectures by Dr. G. G. Henderson, F.C.S., on the "Evolution of the Lucifer Match," and that by Dr. E. J. Mills, F.R.S., on "Water and Water Supply," a subject which during the past summer has been forced somewhat unpleasantly upon the notice of the public. One lecture, to be delivered by Dr. John Young, Professor of Natural History, Glasgow University, entitled "The Medallic Art of Renaissance," seems, if we understand its title aright, to have been more suited for discussion by a Royal Academician than by a professor of natural history. Mr. A. Humboldt Sexton's survey of a century's technical education in Glasgow must doubtless have proved highly suggestive.

**The Stas Memorial.**—The following announcement has been circulated among the subscribers to the Stas Memorial Fund:—"The Committee formed to do homage to the memory of Jean Servais Stas was definitely constituted on December 13, 1892, the anniversary of the death of the illustrious *savant*. During the following month the list of subscriptions was circulated; the money received was deposited in the State Saving's Bank till required. The subscription will remain open till May 1, 1894. The chief object the Committee had in view in appealing to the public was to reprint the works of Stas. This work, from which the Executive Committee does not assume the right to eliminate any important matter, forms three quarto volumes of from 500 to 600 pages each. The first volume includes the memoirs and work specially devoted to the atomic weights; the second volume contains notes and notices, reports, and discourses; the third volume contains posthumous works, especially relating to spectroscopic researches. The edition will be published under the direction of MM. Spring and Depaire. Arrangements have been made to enable the work to be finished within a year. The resources actually at the disposal of the Committee have enabled them to entrust this part of their work in the hands of a competent publisher. What ultimately remains from the subscribed money will go towards the erection of a monument. It will not be disposed of till after the publications are issued. The three volumes of the complete works of Stas will be published simultaneously at the price of thirty francs. Every one who has subscribed a sum of at least twenty francs will receive a copy gratuitously. Subscribers whose contributions are below that amount may increase their subscriptions up to the above sum. The Committee will be obliged if you will communicate this decision to those who may be interested in it. Names of subscribers will be published in an appendix to the last volume."

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Books.—Could any correspondent tell me the best books, editors, and publishers on Coal Gas Analysis and Roman and Portland Cements Analysis?—Enquirer.

## MEETINGS FOR THE WEEK.

Friday, 27th.—Physical, 5. "On Air-Core Transformers," by E. C. Rimington. Two Experiments by W. B. Croft, M.A., on the Rings and Brushes in Crystals, and Electrical Radiation in Copper Filings.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1770.

## FERMENTATION IN THE LEATHER INDUSTRY.*

By JOSEPH T. WOOD.

The science of Bacteriology touches upon the leather industry in the following important points:—

1. Putrefaction.
2. The soaks.
3. Changes in lime liquors.
4. Bating or "puring."
5. Drenching.
6. Fermentation of tan liquors.

I only propose to give a short *resumé* of our present knowledge of the "drenching" process, as this closely resembles ordinary fermentations.

Skins from the bate after washing are placed in vats containing an infusion of bran in water (0·4 to 1 per cent of bran) at a temperature of 30° to 35° C. This ferments vigorously for 18 to 24 hours, with evolution of considerable quantities of gas and the formation of weak organic acids, which have a slight swelling action on the skin, cleanse the pores, and make it in a fit condition to receive the tannin. On examination with a high power of the microscope the liquid is found to be swarming with active bacteria. They are mostly in the form of pairs or dumb-bells, each cell $0·75\ \mu \times 1·25\ \mu$; some form chains. I described (*Journ. Soc. Chem. Ind.*, ix., 27) a method by which the organism causing the fermentation was separated, as it refused to grow in ordinary nutrient gelatin; and lately, in conjunction with Mr. W. H. Willcox, B.Sc., have made a complete examination of the products of the actual fermentation, previous to carrying out a similar research with the pure ferment.

We found the following gases evolved:—

| Gases. | A. | B. | C. |
|---|---|---|---|
| $CO_2$ and $H_2S$ .. .. .. .. | 21·9 | 25·2 | 42·4 |
| $O_2$ .. .. .. .. .. .. .. | 1·0 | 2·1 | 3·6 |
| $H_2$ .. .. .. .. .. .. .. | 53·1 | 46·7 | 28·2 |
| $N_2$ .. .. .. .. .. .. .. | 24·0 | 26·0 | 25·8 |

A is from a vat containing no skins, 1—2 days.
B from a vat containing skins, 2—3 days.
C from a vat containing skins, 3—4 days.

The $H_2S$ is present only in small quantities (1—2 per cent).

The principal acids found were acetic and lactic, accompanied by small quantities of formic and butyric acids.

The following Table shows the quantities found in an experimental drench per 1000 c.c.:—

| | Grms. |
|---|---|
| Formic acid .. .. .. .. | 0·0306 |
| Acetic acid.. .. .. .. | 0·2402 |
| Butyric acid .. .. .. .. | 0·0134 |
| Lactic acid.. .. .. .. | 0·7907 |
| Total .. .. .. | 1·0749 |

We find in actual work that the quantity of acid produced varies from 1 to 3 grms. per litre. We found that an unorganised ferment, "*cerealin*," changes the starch of the bran into glucoses and dextrin; the bacteria then ferment the glucoses, splitting them up with evolution of gases and formation of acids.

The bacteria causing the fermentation have no action on the cellulose of the bran nor on the skins, as some bacteria in the bate have; in every case where the skin is attacked it is by putrefactive or gelatin liquefying bacteria introduced from the bate, or in specially favourable circumstances (hot sultry weather) developing from germs always present in the atmosphere. The gases evolved have only a mechanical action on the skin, floating and distending them, and so enabling them better to take up the acids. In carrying out this work we discovered a delicate test for lactic acid.

The presence of lactic acid was shown in the following manner:—10 c.c. of the liquid were placed in a small distilling flask along with 2 c.c. strong $H_2SO_4$ and about 0·5 grm. potassium chromate in a little water. This was distilled and the vapours received in a test-tube surrounded by cold water; on adding magenta solution decolourised by $SO_2$ to the liquid in the test-tube, a red colour was produced by the aldehyd formed from the lactic acid; aldehyd was also recognised by its smell. We find this an exceedingly delicate test for lactic acid, and as far as we know it is quite new in this form.

For 10 c.c. of liquid to be examined we find 2 c.c. strong $H_2SO_4$ and 1 grm. of potassium chromate to be the best proportions. Formic, acetic, propionic, butyric, valerianic, succinic, malic, tartaric, and citric acids do not give the reaction.

In conclusion, there are no doubt other organisms capable of fermenting a bran infusion in a somewhat similar way, and the work of isolating and separately examining their life history and products yet remains to be done.

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* Abstract of a Paper read before the British Association (Section B), Nottingham Meeting, 1893.

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## THE VOLATILITY OF PYROPHOSPHORIC ACID.

By GEORGE WATSON, F.C.S.

Orthophosphoric acid, according to the text-books, is dehydrated into pyrophosphoric acid at a temperature of 215° C., and into metaphosphoric acid at a red heat, at which temperature the latter is slowly volatilised, but no statements regarding the volatility of pyrophosphoric acid have, to my knowledge, been recorded.

The possibility of the latter being volatile suggested itself to me from noticing the behaviour of a strong solution of orthophosphoric acid during concentration. About 2 kilos. of the "ortho" acid, having a specific gravity of 1·750, was being heated in a platinum basin, in order to expel a trace of nitric acid which it contained. The basin was heated by means of a Fletcher's small ring radial burner; the temperature, obviously, never at all approaching redness. Nevertheless, when all the free water had been driven off (which could be approximately told from the bubbles of evolved steam becoming very much smaller in size) a bluish white smoke began to rise from the acid. On holding a test-tube, wetted externally, in this smoke for a few minutes (having first turned off the gas in order to prevent the projection of any drops of acid on the tube) the film of water was found thereafter to contain a very perceptible quantity of phosphoric acid. A warmed thermometer on being plunged into the acid indicated a temperature of 290° C. at the surface; while on being thrust to the bottom, the mercury rose to 330° C., upon which the thermometer was withdrawn. From this observation it was evident either that metaphosphoric acid was formed at a temperature of 290° C. and was volatile at that temperature, or that the acid volatilising was the "pyro" one.

Before proceeding to examine the question systematically, a tentative experiment was made by exposing 19·362 grms. of phosphoric acid, of 1·750 sp. gr., in a platinum capsule to a moderate heat over a radial burner, the gas being turned down till the flame was about 2 c.m. from the bottom of the capsule. The amount of orthophosphoric acid contained in the acid used was 90·20 per cent, from which it is calculated that the weight of "pyro" acid obtainable from the 19·362 grms. taken should be 15·860 grms. After one and a half hour's heating the weight of the residue was found to be 14·450 grms. and after other two hours heating 14·295 grms., thus showing a loss of about 1·5 grms.

A series of experiments was then performed as follows:—

A small quantity, usually about 0·5 grm., of the syrupy phosphoric acid mentioned above was weighed into a platinum capsule, which was then placed in a Rammelsburg air-bath. A thermometer, wound with a strip of asbestos cloth, was fixed into one of the holes in the bath lid, the bulb resting on the tray close to the capsule, while the other hole was plugged with a roll of asbestos cloth. The bath was then placed in a large tin can (a phosphorus tin) and the whole heated by means of a radial burner. With this arrangement the temperature could be kept fairly steady, a few degrees only of variation taking place, but an eye was kept on the thermometer pretty constantly as well during each experiment. Undernoted are the particulars:—

*Experiment* 1.—1·363 grms. of phosphoric acid, heated to 215° C. for five hours, gave a residue weighing 1·172 grms. The calculated weight of "pyro" acid being 1·116 grms., dehydration was therefore incomplete.

*Experiment* 2.—Acid taken, 0·4645 grm.; heated for five and a half hours to 215° C., residue weighed 0·391 grm.; heated next day for another six hours to 225° C., residue weighed 0·389 grm.; calculated weight, 0·3805 grm. Dehydration still incomplete.

*Experiment* 3.—0·5565 grm. phosphoric acid, heated for ten hours for 220—225° C., residue weighed 0·470 grm.; heated other three hours next day to 215° C., residue weighed the same; heated following day for other seven hours to 215° C., weight of residue unchanged. The residue was then converted into magnesic pyrophosphate, which was found to weigh 0·5655 grm.; this is equal to 0·4534 grm. of "pyro" acid, or 0·4992 of the "ortho" form. As the residue weighed 0·470 grm., it follows that the conversion into the "pyro" modification was again incomplete, while the calculated weight of "ortho" acid in the 0·5565 grm. taken being 0·5019 grm., it is evident that no volatilisation had taken place, the slight loss of 2·7 m.grms. being probably due to errors of experiment.

*Experiment* 4.—0·448 grm. acid, heated for seven hours to 230—235° C., residue weighed 0·3735 grms.; heated next day for other seven hours to the same temperature, residue weighed 0·3755 grm. It was then converted into magnesic pyrophosphate, and gave a precipitate of 0·4587 grm.; this is equal to 0·3678 grm. of pyrophosphoric acid, which on subtraction from 0·3735 leaves 5·7 m.grms. of water still present. Calculating the magnesic salt into orthophosphoric acid, we get 0·4049, while the weight contained in the 0·448 grm. taken is 0·4041 grm. This shows no loss by volatilisation.

*Experiment* 5.—0·535 grm. acid, heated to 255—260° C. for six and a half hours, residue weighed 0·427 grm., which on conversion into magnesic salt gave a precipitate of 0·5340 grm. This is equal to 0·4281 grm. of "pyro" acid, or 0·4715 grm. of "ortho" acid, which on deduction from 0·4825 (the weight of $H_3PO_4$ in the 0·535 grm. of acid taken) gives a loss of 0·011 grm.

*Experiment* 6.—0·4 grm. acid, heated to 280—285° C. for seven hours, residue weighed 0·3055 grm.. After heating next day for other seven hours it weighed 0·2905 grm.; other seven hours' heating gave 0·2755 grm. The magnesic pyrophosphate obtained from this weighed 0·3458 grm., which is equal to 0·2766 grm. of "pyro" or 0·3053 grm. of "ortho" acid. The weight of "ortho" acid in the 0·4 grm. taken being 0·3608 grm.; this indicates a loss of 0·0555 grm.

*Experiment* 7.—0·433 grm. acid, heated to 280—285° C. for seven hours, residue weighed 0·3315 grm. The weight of magnesic pyrophosphate obtained from this was 0·4151 grm., which is equal to 0·3328 grm. of "pyro" acid, or 0·3665 grm. of "ortho" acid. The weight of "ortho" acid taken being 0·3905 grm., a loss of 0·024 grm. is shown.

*Experiment* 8.—0·5087 grm. of acid, heated to 285—290° C. for the following periods of time:—

| | | |
|---|---|---|
| 3 hours. | Residue weighed | 0·4002 grm. |
| 6 ,, | ,, ,, | 0·3702 |
| 7 ,, | ,, ,, | 0·3610 |
| 3 ,, | ,, ,, | 0·3442 |
| 7 ,, | ,, ,, | 0·3150 |

On conversion into magnesic pyrophosphate, a precipitate weighing 0·3915 grm. was obtained. This equals 0·3139 grm. of "pyro" acid, or 0·3456 grm. of "ortho" acid. Deducting this from the weight of "ortho" acid taken (0·4588 grm.), a loss of 0·1132 grm. is indicated.

An experiment at a temperature of 290—300° C. was also made, and the residue tested for "meta" acid by dropping a solution of baric chloride on it and allowing to stand. A small quantity of "meta" was indicated.

From these experiments I conclude—

(*a*) That orthophosphoric acid is not completely dehydrated into pyrophosphoric acid at temperatures below 230—235° C.

(*b*) That orthophosphoric acid is completely converted into the "pyro" modification at a temperature of 255—260° C., the pyrophosphoric acid being volatile at the same temperatures. Hence it is probable that the temperatures of complete formation and of volatility may be identical; in which case orthophosphoric acid will be analogous to orthoboric acid, which is dehydrated into metaboric acid and slowly volatilised at a temperature of 100° C. (see Roscoe and Schorlemmer, "Treat. on Chem.," vol. i., p. 552).

(*c*) That metaphosphoric acid is on the verge of formation at temperatures about 290—300° C.

## BORON-EISEN.

By H. N. WARREN, Research Analyst.

SILICON-EISEN, chromeisen, alumin-eisen, zinc-eisen, and various other ferro-compounds, are all familiar names, either in the works or laboratory; there still, however, remain gaps to be filled, as in organic regions; one of which, namely, the boron compound, which has lately been successfully procured, is now being further experimented with by the writer, and to which the name boron-eisen has been given, signifying boron-iron.

Boron, unlike most other elementary substances, presents so much difficulty in its estimation that, when present in small quantities, it is too often entirely overlooked; its slight affinity also for other elements presents a grave difficulty in obtaining a regulus; not unfrequently have the buttons procured from the dry assay of iron ores that have been performed under my notice, when subjected to analysis, revealed a total of one or two per cent wanting, and in most cases where borax had been employed as a flux the difference has been found to be boron.

The first preparation of this substance of a definite character was brought about by the addition of a solution of borax to one of ferrous chloride; the white precipitate of ferrous borate thus obtained being pressed to free it from adhering water, and after thoroughly drying, reducing it with an equivalent proportion of carbon in plumbago crucibles. In this way boron from 4 to 5 per cent enters into union with the iron, producing a compound breaking with the fracture of metallic manganese, and presenting sufficient hardness to readily scratch glass, at the same time being with difficulty soluble in acids; the melting-point of the compound approaching that of cast-iron.

A more economical method has since supplanted the former—by reducing ferric carbonate, or oxide, in admixture with boron oxide and charcoal. In this, as in the former method, a number of minute precautions are necessary in order to obtain the desired compound, which if performed dexterously results in the boric oxide gradually reducing and alloying with the iron. The most peculiar property of this compound is its great predominancy when in admixture with large quantities of iron; one ounce of the boride thus melted with about two pounds of iron causes the whole to break with almost an analogous fracture of the boron compound itself, whilst at the same time it contains but the fraction of a percentage of boron. The boron iron thus produced casting more soundly, expanding slightly, and being free from blowholes.

The average of several analyses of the compound prepared at high temperatures are the following:—

| | |
|---|---|
| Iron .. .. .. .. .. .. | 94·08 |
| Boron .. .. .. .. .. .. | 4·02 |
| Combined carbon . .. .. | 1·50 |
| Phosphorus .. .. .. .. .. | 0·09 |
| Sulphur.. .. .. .. .. .. | 0·31 |
| Silicon .. .. .. .. .. .. | trace |
| Manganese .. .. .. .. .. | trace |
| | 100·00 |

Several other curious compounds of boron not hitherto dealt with will shortly appear.

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## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 195).

### *The Photograph of the Spectral Region beyond the Wave-length* 185·2 $\mu\mu$.

According to the foregoing proofs the most refrangible rays of aluminium had entirely lost their energy in a stratum of air of 17 metres in thickness; at 2 metres of air they had left upon the plate an impression capable of being developed, and at a distance of the spark from the plate a good photograph. Their photographic action and its intensification were not in consequence of a heightened intensity of the spark, but of the diminished resistance which the rays encountered on their way to the plate. The spark was quite sufficient, but the energy of the rays was defective. When they had passed through a great length of air, their photographic efficacy at its entrance into the silver particles of the plate was no longer strong enough to set up its decomposition to a sufficient degree. The preservation of the energy of the rays was therefore the point upon which a better result must be founded.

In all probability, even at the smallest focal distance which I have employed, the loss of energy of the rays was very considerable in consequence of various hindrances which they encountered on their way. If this loss could be diminished further success was in view. That such diminution was possible was beyond all doubt. Even the removal of the air which still intervened between the spark and the plate (though only in a stratum of moderate thickness) promised appreciable advantages. But the air was not the sole obstructive absorbent which the rays encounter on their way. Quartz absorbs the most refrangible rays to a perceptible extent (L. Soret, *Arch. des Sciences Phys. et Nat.*, lxi., 332—334, 1878); also glycerin (W. A. Miller, *Phil. Trans.*, clii, 871, 1862), with which the halves of my quartz prism were corrected; and also gelatin, even in a thin stratum, obstructs them visibly (Soret, *Arch. des Sc. Phys. et Nat.*, III. period., x., 453—455, 1883).

If these hindrances existed, and if their renewal or their great reduction was possible, a further increase of photographic energy would be secured.

The photographic effect is not merely a function of the energy of the rays—it depends above all on the behaviour of the sensitive plate. The more unstable the chemical combination of the sensitive constituents of the coating of the plate, the more its loosening during the action of the rays is assisted (Sensitiveness, H. W. Vogel, "Handbuch der Photographie," IV. edition, 1890, pp. 172, 193, 208), the more rapid is its decomposition on exposure. If it were possible to assist in this manner the more refrangible rays, the prospect of success would become more favourable.

Delicate details in a photograph, faint luminous impressions, require a plate quite free from any veil. They become turbid, doubtful, and often disappear again if the ground issues from the developing-bath not clear as glass, but covered with a grey layer.

As already mentioned, this case occurred regularly in my proofs on prolonged exposure. The dispersed light from the interior of the apparatus, the cause of this veil on the plates, is composed of rays of all degrees of refrangibility; but only those for which the plate is most sensitive have a veiling action. These, with gelatin plates and spark light, are the rays of less refrangible ultraviolet,—those, therefore, which are not wanted for my purposes. If I could keep them out of my apparatus my proofs would be still further the gainers. Not merely was there secured greater clearness for the more delicate impressions, but the design of the entire proof was improved.

This consideration led to a series of researches which had to precede the resumption of my original work. These preliminary operations consisted in:—

1. In ascertaining the influence of all absorbents which come into play in the photographic action of the most refrangible rays of spark light.
2. In the utilisation of the results thus obtained for the creation of better means of observation for the spectral region in question.

The only exception here was glycerin, which could be disregarded, since the double prism of the apparatus works correctly without being cemented together. The glycerin was only to prevent the loss of light occasioned by the reflexion which arises on the planes of the two single prisms if left uncemented.

The absorptive behaviour of quartz and gelatin with the most absorptive rays of aluminium has certainly been very carefully determined by Soret. But he has only employed the eye-piece. His results do not, therefore, necessarily agree with those of the photographic plate.

The relations of brightness of the wave-lengths, as ascertained by Soret, according to the fluorescence have always a relative value.

(To be continued.)

**Influence of Organic Solvents upon the Rotatory Power of the Tartaric Ethers.**—P. Freundler.—All the solvents, except carbon disulphide, act in the same direction upon the chemical molecule of the tetra-substituted tartaric ethers. Hence Biot's law is confirmed, and the variations of the rotatory power furnished by certain solvents are due to a dissociation.—*Bull. de la Soc. Chim. de Paris.*

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## ON ERBIA.*

By GERHARD KRÜSS.

(Continued from p. 194).

All the preparations were excellent erbia materials, as appears from the values obtained for $\overset{\text{III}}{R}$. Nilson's preparations Nos. 1 and 2 were united as—

*Erbia Material No.* 9.

This material fractionated in the state of hydroxide by successive treatments with aniline hydrochlorate gave—

*Series* 17.

← Stronger bases.
" Aniline solutions."

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| 164·8 | 165·1 | 166·1 | 167·2 | — |

Weaker bases →.
" Aniline solutions."

| 6 | 7 | 8 | 9 | 10 (Residue). |
|---|---|---|---|---|
| 167·9 | 168·1 | 168·6 | 166·4 | 161·5 |

Fraction 10 of this series was the precipitate remaining from the solution No. 9. It was selected small in weight (about 2 grms.). It is remarkable that there was no increase of the R value in the direction of Yb = 173, but a decline, so that I tested for scandia, but without result.

Fraction 10, in the state of a neutral sulphate, was treated by suspending in it crystals of $K_2SO_4$. There appeared a slightly flocculent precipitate, like an earthy hydroxide, which, after gentle ignition, appeared reddish, and was insoluble in hydrochloric acid. The nature of this body could not be determined on account of its small quantities. But this substance has perhaps occasioned the decrease of the R value in fraction 10, Series 17; for after filtering off this deposit, the liquid was concentrated until $K_2SO_4$ was separated out. It contained an earth, $\overset{\text{III}}{R}=166·7$, and its filtrate, $\overset{\text{III}}{R}=168·6$.

For the further elaboration of fractions 1 to 9, Series 17, 1 and 2 were united as substantially identical. Then the most feebly basic portion of a fraction is first eliminated by treatment with aniline hydrochlorate and transferred to the nearest fraction on the side of weaker basicity; that is, the aniline precipitate from fraction (1+2) can be transferred to fraction 3, the precipitate from the present fraction 3 to fraction 4, and, lastly, the aniline precipitate rom fraction 8 to fraction 9,

The reverse was now taken in order to bring the more strongly basic constituents of one fraction into the adjacent fraction on the side of stronger basicity, *i.e.*, the aniline solution from fraction 9 was brought over to fraction 8, and that of fraction 4 to fraction 3, &c. The analysis of the fractions then showed—

*Series* 18.

Stronger bases ←. →

| (1+2) | 3*a* | 3*b* | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| 162·9 | 163·3 | 164·7 | — | 165·9 | 167·2 | 166·8 | 168·3 | — |

Fractions 1+2 and 3*a* of Series 18 were excluded in the further elaboration of the material for Er = 166 or 167, as being too strongly basic. It must be remarked that the determinations of the equivalents of fractions 5 to 8 (Series 18) had given values which in fact might lead us to conjecture the non-existence of an erbium with $\overset{\text{III}}{R}=166$ or 167 to 168. This is the same phenomenon to which attention was called above on the decomposition of the erbia materials Nos. 6 and 7.

In order in the fractions 3*b*—9 (Series 18) to bring from every fraction small quantities of the more strongly basic oxides to the corresponding side, and more feebly basic oxides to the other side of the series of fractions, these earths were worked up by aniline precipitations and aniline solutions on the same system as fractions 1—9 (Series 17), After carrying out these operations the analysis of the earths gave the following values:—

*Series* 19.

← Strong bases.

| 8 (dissolved) | 3*b* | 4 | 5 |
|---|---|---|---|
| | 165·5 | 167·4 | 165·1 |

Weak bases →.

| 6 | 6/7 | 7 | 7/8 | 8 | 9 |
|---|---|---|---|---|---|
| 170·2 | 172·5 | 168·3 | — | 167·1 | 168·5 |

If in the fractions 5 to 8 of Series 18 there had been present an erbium with a constant $\overset{\text{III}}{R}$ between 166—168, this must have come in evidence still more in the values found for the fractions of Series 19 than in Series 18. Here, also, as on working up the material No. 8, it was found that as other earths are approximately removed from the erbia material the earth with $\overset{\text{III}}{R}=166—168$ becomes relatively unstable in contact with aniline hydrochlorate. The fluctuations in the values of the so-called atomic weights which could not be ignored appear considerably stronger in Series 19. To this point we shall return in the sequel.

(To be continued.)

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* *Zeitschrift fur Anorganische Chemie.*

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## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending September 30th, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* General A. De Courcy Scott, R.A.,
*Water Examiner, Metropolis Water Act*, 1871.

London, October 9th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples three were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

The meteorological conditions during the month of September have been of an entirely abnormal character. An excess of bright sunshine and high temperature have stimulated the fluviatile vegetation on which the purity of running streams in great measure depends, and have promoted the oxidation of the traces of organic matter always present in river and lake water. The rainfall, as registered at Oxford, has been remarkably small. The mean rainfall of September, from an average of twenty-five years, is 2·66 inches, whereas the actual rainfall has only been 0·57 inch, showing a deficiency in the month of over 2 inches, and of no less than 3·64 inches for the four months June to September. This deficiency of rain has tended to increase the organic purity of the river, as little or no peaty colouring matter has been washed into it from the collecting area.

How little impurity has been present will be seen from the following table, in which a comparison is shown between the average composition of the five Thames-derived waters for last month with that of the same waters in September, 1892, on which occasion we spoke of the composition and purity of the waters as being "entirely satisfactory."

*Comparison of the Averages of the Five Thames Supplies for the Months of September*, 1892 *and* 1893.

| | Common salt per gallon. | Nitric acid per gallon. | Oxygen required per gallon. | Organic carbon per gallon. | Colour. Brown. Blue. |
|---|---|---|---|---|---|
| | Means. | Means. | Means. | Means. | Means. |
| Sept., 1892 | 2·195 | 0·947 | 0·043 | 0·083 | 15·1 : 20 |
| „ 1893 | 2·163 | 0·570 | 0·026 | 0·057 | 12·2 : 20 |

It is not probable that so exceptional a state of things will last much longer, and as cold, wet weather comes on, a slight increase of vegetable organic matter and peaty colouring matter may be expected.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

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### ON THE

## ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 196).

### Resorcinol ($C_6H_4(OH)_2$).

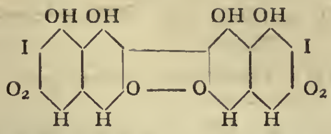
A quantity of the precipitate obtained by the action of iodine on resorcinol was prepared under conditions similar to those set up in the case of the red-violet phenol precipitate (60° C.). In this case only a small proportion of the precipitate was obtained until after acidification. The precipitate was of a dark purple red colour, and of brittle character when dry. It was powdered and boiled direct with chloroform as long as anything dissolved out. The portion dissolved out by the chloroform was very little, and was neglected.

The remainder of the precipitate from the chloroform treatment was almost entirely insoluble in carbon disulphide. It was therefore cautiously heated at a temperature of about 350° C. until it was deemed to have lost all its "encluded" iodine. It was then taken for analysis.

Total iodine:—
Quantity taken =0·1580 grm.
Silver iodide found=0·1105 „ =37·78 p.c. iodine.

Combustion of same:—
Quantity taken =0·1309 grm.
Water found =0·0172 „ = 1·46 p.c. hydrogen.
Carbon dioxide found =0·1762 „ =36·70 „ carbon.
By difference .. .. =24·06 „ oxygen.

Those results may be represented by the formula $C_{20}H_8I_2O_{10}$, or constitutionally thus:—



Theoretical:—
C =36·25
H= 1·21
I =38·36
O =24·18

The high percentage of carbon found was no doubt due to slight decomposition, as the result of heating.

A second batch was prepared with the following proportions:—1 grm. resorcinol, 1·2 grms. caustic soda in 600 c.c. of water at 60° C. The precipitate was similar in appearance to the one just treated of. It was boiled with chloroform in successive portions till nothing more dissolved out. The portion soluble in chloroform, which was very small, was recovered, dried, and the iodine estimated.

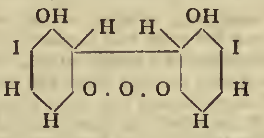
Total iodine of the chloroform-soluble portion:—
Quantity taken =0·1059 grm.
Silver iodide found=0·1560 „ =79·66 p.c. iodine.

The remainder of precipitate, insoluble in boiling chloroform, was cautiously heated until the "encluded" iodine was driven off. (This portion was also insoluble in carbon disulphide). It was then taken for analysis.

Total iodine:—
Quantity taken =0·1072 grm.
Silver iodide found=0·1034 „ =52·11 p.c. iodine.

Combustion of same:—
Quantity taken =0·0844 grm.
Water found =0·0138 „ = 1·81 p.c. hydrogen.
Carbon dioxide found =0·0908 „ =29·33 „ carbon.
By difference .. .. =16·75 „ oxygen.

Those results may be represented by the formula $C_{12}H_8I_2O_5$, or constitutionally thus:—



Theoretical:—
C =29·63
H= 1·64
I =52·26
O =16·47

This latter batch would agree fundamentally with that obtained by M. and V., who reported a total iodine percentage for the resorcinol precipitate of 72·48, and assumed it to be the potassium salt of di-iodo-resorcinol-iodide, which they represented thus:—

$$C_6H_2I_2{<}^{OK}_{OI} .$$

It is evident from the analyses I have submitted that the precipitate consisted of a mixture of a mono- and tri-substituted compound.

The first batch, whose total iodine percentage was 52·67, probably contained a di-substituted molecule, together with the compound whose full analyses I have given.

(To be continued).

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**Chaloner Testimonial.**—Mr. George Chaloner, F.C.S., having resigned the position of Lecturer on Chemistry at the Birkbeck Institution, which he has held for a quarter of a century, it is thought that many of his old students and friends will be glad to combine to present him with some mark of good-will and esteem on the occasion of his retirement. With this view a Committee is being formed to consider the form of the Testimonial, to receive subscriptions, and to make arrangements for the presentation. It being the desire to make the Testimonial as largely representative as possible, it is suggested that the subscriptions should be limited to sums not exceeding one guinea. A preliminary meeting will be held on Tuesday, October 31st, 1893, at 43 and 44, Holborn Viaduct, E.C., at 7 p.m.—E. Godwin Clayton; Herbert Trewby.

# LAWS AND NATURE OF COHESION.

## Part II.

By **REGINALD A. FESSENDEN**, Lafayette, Ind.

In a previous note (*Science*, July 22, 1892, and Chemical News, lxvi., 206), a number of reasons were advanced for believing that cohesion is due to an electrostatic force, and it was shown that the results predicted by such a theory agree very closely with the results of experiment.

This theory was, however, only extended to the phenomena of rigidity, elasticity, and tensile strength. It was purposed to follow it with another note on the phenomena of conductivity, surface tension, solution, refraction of light, and compression of gases. Pressure of other work and the necessity of making experiments to determine some doubtful points will prevent such publication for some time, and it was therefore judged best to give a short preliminary statement of a few of the results so far obtained.

1. *Relative Closeness of the Atoms.*—It appears to be generally considered that the atoms are at distances from each other which are large in comparison with their diameters, even in the solid state. As an example of the extent of this belief may be mentioned the fact that in a recent article on magnetism Mr. Steinmitz made the statement that Professor Ewing's theory could not be correct, unless the atoms were close together, but as they were far apart, his theory must be wrong. This conclusion has not been attacked up to the present time. But the facts are that all our evidence points the other way, and it is almost absolutely certain that in the solid state the distance between the centres of two neighbouring atoms is almost the same as their diameters.

For instance, from Van der Waals's equation we have, at the critical point:—

Volume of gas = 12 times the volumes of the atoms themselves, or, the distance between the centres of two atoms is 2·3 times the diameter of a single atom. And this is just at the critical point, so that from the curves of volume, pressure, and temperature, the solid elements must have a volume of, at the most, six times that of the atoms themselves, reducing the distance between centres to 1·8 times the atomic diameter.

Again, when a body is at absolute zero it is extremely difficult to conceive why the atoms, having no kinetic energy and the cohesive force still in existence, should not join together as closely as is possible, *i. e.*, till they touch. (We may discard the old "force point" atom as obsolete and without reason for existence, all modern research and theory being in favour of the idea that atoms have most exact and well-defined boundaries).

If, then, the atoms of silver in the solid state at 0° C., say, were very far apart, then, since we know its change of volume is very slight down to about –200° C., there must be a most remarkable and sudden change at some point in the last 73°. But this is not to be believed, for it is impossible for any such violent change in the space occupied by the atoms to take place without some change in the conductivity of the metals. And we know from the researches of Dewar and others that the curve of resistance is a straight one, and cuts the axis of temperature at absolute zero, if produced.

On the other side, after considerable search, there does not appear to be any reason for believing that the atoms are widely separated in a solid, and the writer would be glad to know of any such reason, other than the fact that certain mathematicians have seen fit to make the supposition because it renders some of the work on surface-tension, &c., a little easier to handle.

There is, it is true, one class of facts which has hitherto been looked upon as evidence of this nature, but which must, by all the laws of evidence, be considered as proof of the comparative closeness of the atoms instead of the opposite. For if, according to two theories, a certain effect should follow certain conditions, and according to one theory there is no assignable limit to the effects, while according to the other there is a well-defined limit, then if out of a great number no effect is found to pass the well-defined limit, all the evidence is in favour of the latter theory.

The phenomena referred to are the facts that some of the elements can combine with other elements to form compounds having a less atomic volume than the element itself. For instance, 45·5 c.c. of potassium combine with one equivalent grm. of chlorine to form one equivalent grm. of KCl, having a volume of only 37·4 c.c. But if we suppose, as we have every reason for believing is the fact (witness the great advances which have been made in organic chemistry, due to the theory that the carbon atom has the form of a tetrahedron, and the still more recent work on nitrogen), that the atoms have regular geometric forms, then it is inconceivable that the facts should be otherwise than they are.

For, suppose that the potassium atom has the form of a sphere, then, when in the free state, as it is homogeneous, every atom must be similarly situated with respect to every other atom, *i.e.*, the atoms must have the position shown in fig. A. It is easily shown that by the combination with the potassium atoms of an element whose atomic volume is less than 3·4, the resultant volume would fall to 32, the atoms taking the position shown in fig. B (shown in two dimensions only, it should be in three), the original volume of the potassium alone being 45·4.

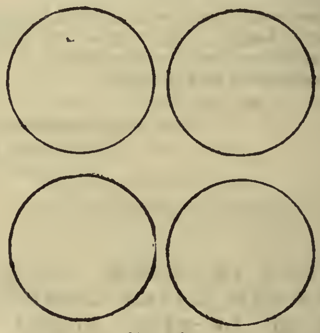


Fig. A.

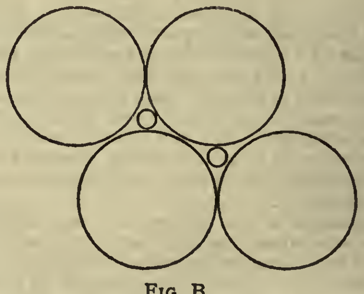


Fig. B.

Similarly, it may be seen that the potassium atoms can combine with an element of atomic volume 18 without any increase in bulk beyond the 45·5 of the potassium alone. Any combination with an element of less atomic volume than 18 would be followed by a diminution in volume. All this is on the supposition that the atoms of the combining element are spherical. If they are of any other form the diminution in bulk on the combination of an element of a given atomic volume would be greater. For instance, potassium could combine with an element whose atoms are of cubical form, and be reduced in bulk to an atomic volume of 32 if the volume of the combining element were 4·33 instead of 3·4, as would be the case if the element were spherical.

It is to be noticed, moreover, that this diminution of bulk occurs only when elements of large atomic volume combine with the elements of small atomic volume, *i. e.*, in the case of sodium, potassium, cæsium, and rubidium, and that in no case is the contraction greater than that given by these purely geometric conditions, so that we may discard all theories based on elements having two or three atomic volumes according to the element they combine; it will also be evident that by combining crystallographic data with those derived from volume measurements we have a means, possibly, of working out the stereotomy of all the atoms.

(Note.—In passing it is curious to note that the number of "space nets" into which an infinite number of points (each point similarly situated to every other point) may be arranged is sixty-six, or just the number of the well-defined elements. So that imagination may picture Spencer's homogeneous cloud of atoms splitting up into these different "space nets" arrangements, each kind of net being a different element).

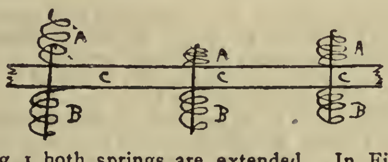
2. *Solution.*—The chief opponent of the disassociation theory of solution is Professor Pickering; and his chief argument against it (for of course the disassociation theory allows the formation of hydrates as well as Professor Pickering's own hydrate theory does) is the fact that while disassociation almost always takes place with absorption of heat, solution generally emits it. This anomaly can be explained very satisfactorily by the electrostatic theory of cohesion. For whether a substance is a solid (or fluid) or a gas depends on whether the fraction

$$\text{I.}\quad \frac{\text{cohesive force of atoms}}{\text{repulsive force due to kinetic energy of atoms} + \text{attraction of atoms for other atoms}}$$

is greater or less than unity. We can thus turn a substance into a gas by either decreasing the numerator or increasing the denominator. The numerator we cannot change. The first term of the denominator we can increase by heating the substance, the second term by placing the substance in contact with a solvent.

In the last case the atoms of the solid part company with each other. But their cohesive force is not lost; it is simply added to that of the solvent, as shown by the increase of surface tension and of boiling-point of a solution over that of the solvent. Since the solvent takes up the stress there is no necessary evolution or absorption of heat. A mechanical simile will make my meaning clear: suppose a spiral spring, A, fixed on a board, C, which when compressed gives out heat from some reversible cause, so that it will absorb the same amount of heat in expanding. This is similar to the behaviour of a gas—when compressed it gives out heat, when it expands again it absorbs heat.

But now suppose a second spring, B, placed beneath the board, C, similar in every respect to the first spring, and its axis a prolongation of that of A. Suppose an iron rod fastened to the bottom of C, extending up the centre of both springs, the rod being somewhat longer than one of the extended springs, and having a hoop on the end of it.



In Fig. 1 both springs are extended. In Fig. 2 the spring A is compressed, heat being given out.

If it is now allowed to expand, the same amount of heat will be absorbed. This latter represents the turning of a solid into a gas by heating it.

But suppose, being compressed, the iron rod is hooked over the top of it. Then when it is let go it will expand and assume the position of Fig. 3. But no heat will be generated in the system, for it is evident that B will give out just as much as A absorbs. If the amount of heat given off by unit contraction of A were greater than that given off by B, the resultant effect would be a cooling of the system. If it were less, the resultant would be a heating. So we see that while the expansion of A by itself would always absorb heat, when it is joined to B the resultant effect depends on B.

Now this is a very fair simile of what goes on when a solid is dissolved in a solvent. The solid loses its stress, which is taken up by the solvent, the result being an increase of cohesion between the molecules of the solvent, producing as a natural consequence increase of surface tension, lowering of the freezing-point, and raising of the boiling-point.

If the added electrostatic strain produces a greater amount of heat in the solvent than the loss of strain in the solid would absorb heat, the resultant would be a heating of the whole solution. Since, when a dissolved substance is plated out by electrolysis, the result resembles the cutting of the iron rod, D, in Fig. 3, there is an absorption of energy or cooling, so that work must be done to plate the dissolved substance out, and the electromotive force necessary to do this, since the ampères are constant for all equivalents, must depend on the rate at which the surface tension varies per withdrawal of unit weight of the electrolysed substance, allowing also for any heating or cooling during the electroplating. It will be noticed that this theory differs in many respects from the ordinary theory of disassociation, but gives in general the same results.

3. *Compression of Gases.*—The ordinary formula for the compression of gases is that of Van der Waals, *i.e.*,—

$$\text{I.}\qquad \left(p+\frac{a}{v^2}\right)\left(v-b\right)=\text{RT.}$$

If the electrostatic theory of cohesion is correct, the equation should read—

$$\text{II.}\qquad \left(p+\frac{a'}{v^{\frac{4}{3}}}\right)\left(v-b\right)=\text{RT.}$$

for reasons evident to those who have read the previous note (*Science*, Aug. 22, 1892).

This is no longer a cubic, and it is pretty certain that the equation for the compression of gases should be one on account of the shape of the pressure-volume curves of carbonic acid gas. But we can transform the above equation, II., into a cubic by putting $a$ no longer as a constant, but equal to a constant multiplied by $v^{\frac{2}{3}}$. The equation then reads—

$$\text{III.}\qquad \left(p+\frac{c\times v^{\frac{2}{3}}}{v^2}\right)\left(v-b\right)=\text{RT.}$$

in which $c$ is the same for all gases. The experimental data agree with this modified equation, as shown by Table I.

TABLE I.

| Substance. | $a \times 10{,}000$. | $v$ (*ab*). |
|---|---|---|
| Diethylamine .. .. .. .. | 355 | 58 |
| Ethyl. acet... .. .. .. | 348 | 55 |
| Ether .. .. .. .. .. .. | 324 | 57 |
| Benzine . .. .. .. .. .. | (438) | 51 |
| Ethyl. form.. .. .. .. | 304 | 48 |
| Chloroform .. .. .. .. | 287 | 44 |
| Acetone .. .. .. .. .. | 273 | 44 |
| Methyl. acet. .. .. .. .. | 248 | 39 |
| Alcohol.. .. .. .. .. | 236 | 37 |
| Ethyl. chlor.. .. .. .. | 227 | 40 |
| $CS_2$ .. .. .. .. .. .. | 219 | 33 |
| $SO_2$ .. .. .. .. .. .. | 123 | 24 |
| $NO_2$ .. .. .. .. .. .. .. | (74) | 19 |

as closely as can be expected.

TABLE II.

| Substance. | $\pi$. | $a$. | $b^2$. | $27\,b^2$. | $\frac{a}{27\,b^2}$. |
|---|---|---|---|---|---|
| Ether .. .. | 36·9 | 324 | 3249 | 87·723 | 36·9 |
| $CS_2$ .. .. .. | 74·7 | 219 | 1089 | 29·403 | 74 |
| $SO_2$ .. .. .. | 78·9 | 123 | 576 | 15·552 | 79 |
| Alcohol .. .. | 62·1 | 236 | 1369 | 36·963 | 63·8 |
| Eth. chl... .. | 52·6 | 227 | 1600 | 43·200 | 52·5 |
| Benzine .. .. | 49·5 | 438 | 2601 | 70·227 | 62·3 |
| Acetone .. .. | 52·2 | 273 | 1936 | 52·272 | 52·2 |
| Eth. acet. .. | 42·6 | 348 | 3025 | 81·675 | 42·6 |
| Chloroform .. | 54·9 | 287 | 1936 | 52·272 | 54·9 |
| Eth. form. .. | 48·7 | 304 | 2304 | 62·208 | 48·8 |
| Meth. acet. .. | 57·6 | 248 | 1521 | 41·067 | 60·3 |
| Diethylam. .. | 38·7 | 355 | 3364 | 90·828 | 39 |
| Nitrous oxide.. | 37·1 | 74·2 | 376·4 | 10·116 | 73 |

This Table shows that $a$ varies as (volume) $^{\frac{2}{3}}$. Two substances do not agree with this theory—benzine and $NO_2$. This is owing to the fact that the data are given wrongly in the Table from which this is copied (*i.e.*, that in Ostwald's "Outlines of General Chemistry"). This is seen by the following facts:—From the cubic equation we find that at the critical point, $\pi$, the critical pressure—

$$= \frac{a}{27\,b^2}.$$

Table II. gives the results of this calculation, and it will be seen that the values for benzine and $NO_2$ do not coincide with the values for $\pi$. As the values of $a$ and $b$ were originally calculated from $\pi$, it is evident that some misprint has crept into the tables, and there is little doubt but that if the correct values for $a$ and $b$ were substituted, they would fall into line, and that in all cases the quantity $a$, in Van der Waals's equation, must be taken as equal to a quantity $c$, which has the same value for all gases, multiplied by the atomic volume to the $\frac{2}{3}$ power.

4. *Electrical Conductivity.*—As before mentioned, linked atoms cannot conduct. If we examine the enclosed cube of the elements, we see that the non-conducting elements are found on sides E and W of the cube, and these are the elements whose atoms are linked or plexed. We can tell this in the following ways:—

1. By their low specific heats. Those who are acquainted with chemical physics will recognise this fact, and the necessary deduction. Briefly, if the kinetic energies of all molecules are the same at the same temperature, then if the sulphur molecule in solid sulphur is triatomic, or has its mass three times that of one atom; then, since all the $\frac{1}{2} m v^2$ s are equal, solid sulphur will only have $\frac{1}{3}$ the specific heat it would have if the molecule were monatomic (provided that no work is spent in disassociating the molecule).

The standard atomic heat is 6·4. The following substances have low specific heats, and are all insulators or poor conductors:—Sulphur, 5·4; phosphorus, 5·4; fluorine, 5; silicon, 3·8; carbon, 1·8.

2. By their vapour densities. If a substance has a biatomic vapour it is not likely that it will be a monatomic solid. The following substances have two or more atoms to the molecule when in the state of vapour:—Sulphur, iodine, bromine, chlorine, selenium, tellurium, phosphorus, arsenic. And these are all insulators or poor conductors; while mercury, cadmium, zinc, and sodium have monatomic vapours and are good conductors.

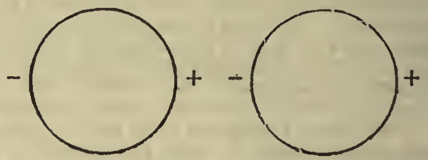
As regards metals in the allotropic state. Allotropic is a word which has been used to cover a multitude of sins. Every time an erring element goes wrong and misbehaves itself by emphasizing some of its previous peculiarities, or developes some new ones, it is stigmatised as "allotropic." For instance, we see it stated that when iron-amalgam is strongly heated the iron left behind is allotropic because it takes fire in the air. But such an action does not show that any new property has been developed, it merely emphasizes a fact already well known, *i.e.*, that iron oxidises when exposed to air. A fine cambric needle will catch fire when held in the flame of a Bunsen burner for a second, and will continue to burn like a match after it is withdrawn. When the iron is in a finely divided state, the surface exposed is greater, and, the oxidation per unit mass being much greater, the temperature of the iron is raised much more, thus favouring oxidation still more.

If, then, we are to use the word allotropic in this sense, we should logically speak of kindling-wood as an allotropic form of timber; for, as fire underwriters know, heavy timber is one of the most fireproof of substances. We might also speak of that form of conscience which large corporations are supposed to possess, as an allotropic conscience.

If, however, we do apply the word allotropic to such forms as Joule's iron, Carey-Lea's silver, &c., then we need another word to express the changes in the physical behaviour of metals which are not due merely to the accenting of known properties, but to the development of new properties, due to the joining of two or more atoms of a metal into one molecule. Polymerism might do, but it does not lend itself easily to use, and for myself I prefer to use the word plex, and to speak of diplexed iodide, triplexed sulphur, and of an element in a plexed form; though I have no doubt that if Clifford were still with us he would say that two-linked and three-linked are good enough for any honest Anglo-Saxon.

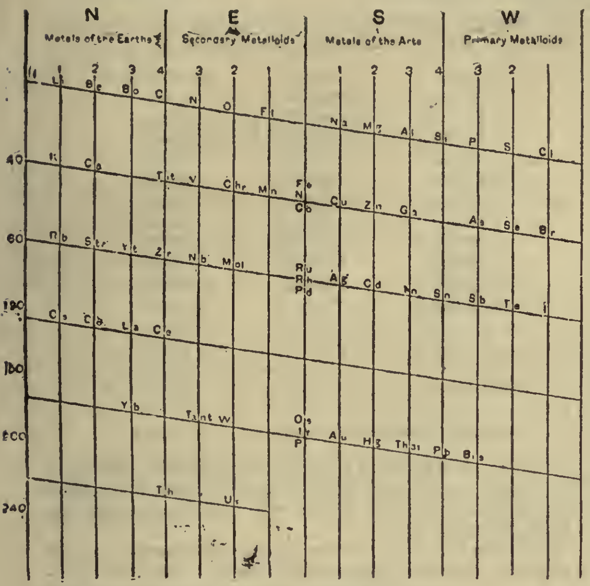
As regards the conductivity of "allotropic" elements, there is no reason to suppose that the conductivity of Joule's iron is different from that of ordinary iron. But when the elements are plexed, as we have seen above, the resistance will be much increased and the temperature sufficiently lowered, because heating increases disassociation nearly as fast as it lessens rigidity, or even in the case of those alloys or elements with negative temperature coefficients, faster.

(NOTE.—With regard to the previous paper, it may be noted that the explanation of the difference between cohesion and chemical combination, that in cohesion the atoms are charged similarly in every way except as regards position, thus—



while if any third substance short circuits the atoms they are left chemically combined, thus—

is also an explanation of a law which will probably be found true in the near future, *i.e.*, no two substances can combine with each other without the presence of a third, thus making all chemical action the result of catalysis, plexed forms of the substances being capable of acting third substances. As regards the shortening of stretched rubber by heating, it is, of course, not to be supposed that the two parts of indiarubber are literally contained one inside a sphere of the other, but that rubber rather resembles a tangled reel of silk embedded in elly. If we consider any element of the jelly, and we see that it is bounded on all sides by threads of silk, and that these will act as the cell-wall of the previous paper,



CUBE OF THE ELEMENTS.

only " more so." The heating of rubber when stretched may be explained conversely by the compression of the jelly-substance by the cell-wall substance.—R. A. F.).

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## THE "BACTERIOLOGICAL" EXAMINATION OF WATER.*

By CHARLES E. CASSAL, F.I.C.

IN a report of the proceedings at a "Congress of the British Institute of Public Health," recently printed and submitted to your vestry, reference is made to certain papers concerning the "bacteriological" examination of water, which were contributed to the "chemistry and climatology" section of this Congress. From the report it appears that the statements made upon the subject were such as to lead to the drawing of erroneous conclusions, and it is therefore important that they should be corrected.

The assertions that the "bacteriological" examination of water "indicates its condition with relation to disease germs," and that the "analytical method" gives the "past history of a water rather than its present condition," are entirely devoid of foundation. The so-called "analytical method" is the only one whereby a knowledge of the actual condition of a water can at present be attained, whatever views may be held as to the degree of efficiency possessed by *any* method for arriving at an accurate knowledge of such condition. There are certain analytical data which, in addition to affording information as to actual condition, in many cases make it possible for an opinion with respect to "past history" to be arrived at; but to conclude from this that the analytical method *only* gives information as to "past history" is obviously and absurdly fallacious. The "bacteriological" method depends upon the more or less successful cultivation of micro-organisms and their spores in certain nutrient media, such as "nutrient gelatin" and meat broth, which must be carried out on a minute portion of a sample of water—the minuteness of the amount used militating strongly against its being representative. It is therefore plain that the method does not of necessity give the actual condition of a water with respect to organisms, but *if successful* merely what may be obtained from the water by a cultivation process, conducted, not in the human body, but in particular prepared substances and under artificial conditions; while the isolation and recognition of disease-producing micro-organisms from samples of drinking water, namely, of organisms of which it can be definitely said that when introduced into the human body they will produce a particular disease, is a problem with which the "bacteriological" method has hitherto shown itself totally unable to cope.

At present the "bacteriological" method affords nothing more than an additional test of a very uncertain and misleading character for the existence of pollution. A water yielding bacteriological results which of themselves would justify its absolute condemnation for drinking purposes would also yield results by the "analytical method" which would necessitate its condemnation. To put the matter in a somewhat different form, every water which could be condemned as unfit for use on the results of a bacteriological test as now capable of application, would also of necessity be condemned on the results of the full "analytical method" including microscopic examination. On the other hand, in the present state of knowledge, it would be the height of dangerous folly to pass a water as pure and fit for drinking purposes upon negative bacteriological results alone, that is, upon results which did not indicate that the water would yield a very large number of "colonies" of micro-organisms on cultivation, or which did not yield what are supposed to be dangerous organisms; whatever may be said about the rashness of franking waters as *absolutely* safe upon negative results of any kind.

The paragraph of the Report next to that containing the assertions which I have traversed, demonstrates in a remarkable way the almost ludicrous uncertainty of the "bacteriological" method. Sir C. Cameron read a paper "on a micro-organism, isolated from drinking water, which is suspected to have caused an outbreak of enteric fever; and in which he brought forward arguments tending to show that a usually harmless germ which is commonly found in water became altered in character and assumed the specific form of the enteric fever bacillus. This has been suspected before as the cause of sudden and otherwise unaccountable outbreaks of enteric fever." If Sir C. Cameron's arguments be accepted as valid, they show that an organism usually regarded by bacteriologists as harmless, and whose presence would therefore not result in the condemnation of the water yielding it, may become highly dangerous under unknown conditions. Further comment is unnecessary.

Vestry Offices, Battersea Rise, S.W.,
September 14, 1893.

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* From a Report to the Vestry of the Parish of St. Mary, Battersea, on the Analysis of Two Samples of Water received on September 1, 1893, from the Vestry's sanitary inspector, and labelled "A" (Lambeth) and "B" (Southwark). (Supplies of the Lambeth and of the Southwark and Vauxhall Companies).

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## THE ATOMIC WEIGHT OF MOLYBDENUM.*

By EDGAR F. SMITH and PHILIP MAAS.

THE present atomic value assigned this element is based upon the results obtained by Dumas (*Ann. Chem. Pharm.*, cv., 84; and cxiii., 23), Debray (*Compt. Rend.*, lxvi., 734), and Lothar Meyer (*Ann. Chem. Pharm.*, clxix., 365). The method pursued by Dumas consisted in the reduction of molybdenum trioxide. Debray also adopted this procedure, but in addition made several experiments upon the precipitation of the trioxide in an ammoniacal solution by silver nitrate. Lother Meyer's value (95·9) is deduced from results obtained by Liechti and Kemp

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* Read before the Chemical Section of the Franklin Institute, September 19, 1893.

(*Annalen*, clxix., 344) in their analyses of the chlorides $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$. The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke ("A Re-calculation of the Atomic Weights," Washington, 1882) expresses the opinion that the most reliable results are those that have been obtained by the reduction of the trioxide. Of the work of Liechti and Kemp, he remarks :—"Traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weight." Rammelsberg (*Berichte d. D. Chem. Gesellschaft*, x., 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be 96·18.

Thinking that additional light could be thrown upon the magnitudes of this constant by proceeding in a different direction, we utilised a reaction first observed by Debray (*Comptes Rendus*, xlvi., 1098; *Ann. Chem. Pharm.*, cviii., 250), which, in the hands of others (Péchard, *Compt. Rend.*, cxiv., 173; *Zeit. f. Anorg. Chem.*, i., 262; Smith and Oberholtzer, *Journ. Am. Chem. Soc.*, xv., 18; and *Zeit. f. Anorg. Chem.*, iv., 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilised with ease in the form of an hydroxychloride—$MoO_3.2HCl$. Numerous trials have demonstrated that the reaction expressed by the equation—

$$Na_2MoO_4+4HCl=2NaCl+MoO_3.2HCl+H_2O$$

is quantitative. We exposed pure anhydrous sodium molybdate (at 150—200°) to the action of hydrochloric acid gas, volatilised the molybdenum trioxide, and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We re-crystallised it many times and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates, or alkaline carbonates—substances that might have been present. The purified salt was dried with extreme care until no further loss in weight was observed. In this anhydrous condition it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6·9780. The balance employed by us was of the Sartorius design.*

The weights of brass and platinum were of Westphal make and had been previously carefully adjusted for this purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes, to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved was first conducted through a U-tube half filled with damp silver chloride; it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride, and finally through clean cotton, after which it was admitted to the combustion-tube, where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150—200° C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilised $MoO_3.2HCl$ was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapour repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made after the boats had remained overnight in the dry desiccators, and showed no appreciable alteration. Barometric pressure and temperature were carefully observed, and all weighings reduced to the vacuum standard. Our results are as follows :—

| $Na_2MoO_4$ in grms. | NaCl in grms. | Atomic weight of Mo. |
|---|---|---|
| 1·14726 | 0·65087 | 96·130 |
| 0·89920 | 0·51023 | 96·094 |
| 0·70534 | 0·40020 | 96·108 |
| 0·70793 | 0·40182 | 96·031 |
| 1·26347 | 0·71695 | 96·087 |
| 1·15217 | 0·65367 | 96·126 |
| 0·90199 | 0·51188 | 96·067 |
| 0·81692 | 0·46358 | 96·077 |
| 0·65098 | 0·36942 | 96·073 |
| 0·80563 | 0·45717 | 96·078 |

Mean .. .. .. .. = 96·087
Maximum .. .. .. .. = 96·130
Minimum .. .. .. .. = 96·031

Difference .. .. .. = 0·099

In our calculations we used the following values :—Na=23·05, Cl=35·45, and O=16. These have been taken from a revised table of atomic weights, published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96·10—the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than to augment the atomic value found. Another cause of a like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result 96·08 obtained by us approaches very closely to the true atomic magnitude of molybdenum.

## NOTICES OF BOOKS.

*Catalogue of Physical Apparatus, &c., Manufactured and Sold by Philip Harris and Co., Ltd.* Edmund Street, Birmingham. 1893.

The authors remark in their Preface that, since they issued a Catalogue of Chemical and Physical Apparatus in 1889, the demand for the appliances needful in technical education has increased to such an extent that they have found it necessary to issue their present special Catalogue of Physical Apparatus. The catalogue extends to 168 pages, and is furnished with 2704 well and clearly drawn illustrations.

Electricity evidently claims the largest share of space. Wimshurst electrical machines are supplied with twelve plates of 26 inches diameter. Almost every form of apparatus required for the study and the application of electricity is duly figured and described, save the appliances of the electric charlatans who now form so numerous and thriving a body. Various forms of calorimetric apparatus are here mentioned, but we do not find Berthelot's calorimetric bomb.

In the section on light several forms of spectroscopes appear; but we see no microscopes, except a model of a compound microscope.

Lanterns have received prominent attention, on account of their increasing use for the illustration of lectures.

Harris and Co. make a speciality of the supply of

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* We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, for the privilege of using this excellent instrument

oxygen, hydrogen, and coal gas, in patent weldless steel cylinders, and give several useful hints for their safe application.

## CORRESPONDENCE.

### BARIUM SULPHATE IN SANDSTONE.

*To the Editor of the Chemical News.*

Sir,—I have to thank Mr. H. T. Mannington for the information communicated by his letter in the Chemical News, vol. lxviii., p. 197. I am in some doubt whether the barium sulphate which he refers to occurs wholly in crevices in the sandstone or partly also in the cementing material which holds the sand-grains together. Perhaps Mr. Mannington can inform me more precisely on this point which I hold to be of some importance. If other gentlemen who have local information to impart on this matter would be so good as to communicate with me, and especially if they would supply me with fully-labelled specimens for analysis and examination, I should feel grateful.—I am, &c.,

Frank Clowes.

University College, Nottingham,
October 21. 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 15, October 9, 1893.

**Relation Between the Precipitation of Chlorides by Hydrochloric Acid and the Lowering of the Point of Congelation.**—R. Engel.—At the congelation-point of a saturated solution of the alkaline and alkaline-earthy chlorides, and the alkaline bromides and iodides, there is a relation between the solubility and the atomic weights of the elements of the molecule. This relation the author purposes to expound in a future paper.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 91.

This number contains merely the *éloges* of the members deceased during the past year,—among whom figures the honoured name of Henry Peligot,—and notices of the prizes awarded to inventors.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., Nos. 17 and 18.

**Assay of Manganese Oxides by means of Oxygenated Water.**—Adolphe Carnot.—Will be inserted in full.

**Natural Manganese Oxides (Part 3), Acerdeses, Hausmannites, and Braunites.** — A. Görgeu. — The author has examined four samples of acerdese, obtained from Ilefeld-in-the-Hartz, hausmannites from Ilmenau, in Thuringen,—which constantly contain zinc oxide in proportions varying from 1 to 8·6 per cent,—and braunite from Saint-Marcel and Schwarzenburg. The specimens from Saint-Marcel are the only manganese ores which contain CoO in a notable quantity.

**Cuprous Phosphide.**—A. Granger.—This compound, $Cu_2P_2$, is obtained in the form of a grey crystalline compound, easily attacked by chlorine and bromine, and readily soluble in nitric acid. In contact with air, it dissolves in ammonia, with the formation of copper phosphate and phosphite.

**A Contribution to the Study of the Salts of Chromium Sesquioxide.**—T. Klobb.—The author describes the double sulphate (chrome and ammonia) and the anhydrous chrome alum. He examines the action of ammonium sulphate upon potassium-chrome alum, and finds that the alkaline chromosulphates or the anhydrous chrome alums crystallise together in all proportions, forming hexagonal tables. The chromotrisulphates crystallise in prismatic needles. The red chromium sulphate appears of a greyish rose colour by day, but green by gas-light.

**Action of Nitrogen Peroxide upon Metals and Metallic Oxides.**—Paul Sabatier and J. B. Senderens.—Manganous oxide (MnO) of a greenish yellow colour, prepared by the action of hydrogen upon the peroxide, is oxidised in nitrogen peroxide at about 350°, yielding manganese sesquioxide. Blackish brown titanium sesquioxide, $Ti_2O_3$, is slowly oxidised at 300°, yielding white titanic acid. Tungstic bi-oxide, $WO_2$, obtained by the prolonged action of hydrogen upon tungstic acid at dark redness, reacts with incandescence below 300°. The product, like that obtained in air, is yellow tungstic acid, $WO_3$, mixed with a little of the blue oxide, $W_2O_5$. Vanadium sesquioxide, $Va_2O_3$, is oxidised at from 300° to 400°, and entirely converted into brownish yellow vanadic acid, $V_2O_5$. Cuprous oxide, $Cu_2O$, is transformed at 300° into the black oxide, CuO. *Metals.*—Metals in the state of filings or reduced by hydrogen are oxidised if heated in nitrogen peroxide almost as in air. With zinc the oxidation begins at 300°. Magnesium filings do not react below dull redness, when a very brisk combustion is set up. Aluminium filings are scarcely attacked at 500°. Lead is slowly oxidised at 200°, and yields a white basic nitrate. Sodium does not oxidise in the cold, and in heat the oxidation is very slow. Copper reduced by hydrogen is converted into black oxide at 250°. Reduced nickel, cobalt, and iron burn with incandescence at the common temperature in nitrogen peroxide, where they are more pyrophoric than in air. The products are $Fe_2O_3$, $Co_4O_5$, and nickel protoxide slightly mixed with sesquioxide. On operating at the ordinary temperature upon reduced copper, and in special conditions upon cobalt, nickel, and iron, we obtain totally different results, which form the subject of the next paper.

**A New Class of Compounds—the Nitro-metals.**—Paul Sabatier and J. B. Senderens.—Nitrogen peroxide, pure and dry, may be fixed in the cold upon certain metals recently prepared by the reduction of their oxides, forming compounds which the authors name *nitro-metals.* These formations have been observed in the cases of copper, cobalt, nickel, and iron. The copper compound has the composition $Cu_2NO_2$. It is a maroon-coloured mass, permanent in dry air in the cold. The reactions of this compound take place as if the nitrogen peroxide were merely in juxtaposition with the copper, each acting on its own account. This neutrality of chemical properties approximates to that of the metallic carbonyles obtained from iron and nickel. Nitro-cobalt, $Co_2NO_2$, is a black powder. The composition of nitro-nickel is similar. Nitro-iron is obtained with much more difficulty, and the authors can merely affirm its existence.

**Polarimetric Observations.**—J. A. Le Bel.—This paper does not admit of useful abstraction.

**Certain Derivatives of Methyl-gallate and Dibromgallate.**—Alex. Bietrix.—The author has obtained the bismuth methyl-gallate, the lead methyl-gallate, the lead methyl dibrom-gallate, and the triacetylic methyl dibromgallate.

**Certain Symmetrical $\beta$-diketones of the Aromatic Series.**—A. Béhal and V. Auger.—This extensive paper does not admit of useful abstraction.

**Bismuth Sub-gallate (Dermatol).** — M. Causse.—This compound, $C_7H_3O_5Bi.2H_2O$, is obtained in small lemon-yellow crystals insoluble in water, but soluble in the mineral acids. It is little affected by air and light.

**A Process for the Synthesis of the Benzenic Carbides.**—A. Brochet.—To effect the combination of the carbides the author proceeds as follows:—A quantity of crystalline benzene is mixed with hexylene, and agitated with 10 per cent of sulphuric acid at specific gravity 1·767. The two liquids blacken strongly. When the first reaction is completed, and after cooling, we add successively fresh portions of the ethylenic carbide, constantly stirring. We may thus introduce into the hexylene half the weight of the benzene employed. Care must be taken to renew the acid at least once at the end of the operation to ensure the total disappearance of the hexylene. There must be no further rise of temperature. We decant off the upper stratum, which is washed first with water and then with caustic soda. The benzene is easily expelled by reason of the great difference between the boiling-points of this liquid and of the product obtained. We obtain, thus, hexylbenzene equal in weight to the hexylene employed. The yield is about 50 per cent.

**Preparation of the Amides in General.**—A. Verley.—The author distils a mixture of the sodium or potassium salt of the acid the amide of which is required, and of the hydrochlorate of the base which is to enter into the reaction. The ammoniacal base which takes rise is at once split up into water and the corresponding amide. The yield is theoretical.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Margarate of Ammonia.**—I shall feel greatly obliged for any particulars as to how I can make anhydrous margarate of ammonia. Kindly say if it is soluble in cold water. I need it for purposes of experiment. I have read in some work on the human body that it is contained in the sweat exuded from the system and can be made artificially by the action of ammoniacal vapour on olive oil, that it melts at 140°, and is soluble in alcohol, but not in water.—W. Page.

Chemist, late Manager of a well-known German colour factory, wishes to sell his experience in Colour-making. Over 100 Receipts, many of them really celebrated. Zinc-yellow, Chrome-yellow, Satinette, Vermilion imitation, Aniline Lakes for Typography and Lithography, Paperhanging, and Satin-paper.—Address, C. M., Chemical News Office, Boy Court, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

VOL. LXVII., No. 1771.

## THE VOLUMETRIC ESTIMATION OF LEAD.

By A. P. LAURIE, M.A.

IN the course of some experiments for the Home Office I found it necessary to determine rapidly the amount of lead present in a large number of solutions containing free hydrochloric acid.

The amount of lead to be determined was small, varying from about 0·05 to about 0·005 grm. I determined after several trials to use the direct estimation by titration with bichromate of potash, using nitrate of silver as an indicator, which is described on page 348 of Crookes's "Select Methods in Chemical Analysis" (Second Edition).

In the first place, I found that the behaviour of the indicator was affected by the presence of chlorides. On adding a drop of the solution to a drop of nitrate of silver, on a white plate, before the bichromate is in excess, a white precipitate of chloride is formed. As soon as a little excess of bichromate is present, the white precipitate of chloride is dyed yellow, so that the end of the reaction is indicated, not by the usual pinky colour, but by the yellow tint of the chloride.

The sensitiveness of this indication is affected by the amount of chloride present in the liquid to a certain extent. If very little chloride is present, the amount of precipitate formed is too small to show the colouration distinctly, and if too much chloride is present the large quantity of the precipitate conceals the effect of the dye.

To obtain the most sensitive reaction, the amount of chloride present should be equivalent to from 0·5 to 0·2 grm. of sodium chloride in 100 c.c.

Under these conditions, 3 parts of bichromate in 1,000,000 parts of water will produce a perceptible change of tint in the chloride of silver precipitation.. In fact, the reaction is, I think, more sensitive than the pink colouration, where no chloride is present.

In estimating the lead I made use of a solution of bichromate which was made up to approximately precipitate 0·002 grm. of lead per 1 c.c. of solution, and I standardised it against pure lead.

One serious practical difficulty is the obstinate way in which the lead precipitate remains floating in the liquid. This is fatal to the method, as any lead chromate taken up with the drop of liquid seems at once to stain the silver chloride, and so render the indicator useless. The best way to get over this difficulty is to add most of the bichromate necessary to precipitate the lead, and gradually raise the liquid to boiling with frequent stirring. This will cause most of the chromate of lead to settle, merely leaving a little floating on the top. On touching the surface of the liquid this floating precipitate is repelled in all directions, and a little liquid can be withdrawn by means of a capillary pipette (made by drawing out a piece of glass tubing), and blown out into the drop of silver. The fresh precipitate formed on adding more bichromate will usually settle on stirring without much difficulty. The precipitate ceases to form just a little before the yellow reaction appears.

In order to obtain results which agree one with another, certain precautions must be taken. The presence of large quantities of other salts in the liquid should be avoided; the liquid, if acid, must be carefully neutralised; and sodium acetate must be added before titration. In standardising the solution, I dissolved the pure lead in as little nitric acid as possible, added ammonia till a slight permanent precipitate was produced, and then added a little sodium chloride and some potassium acetate. The amount of potassium acetate added was about twice the weight of the lead present. I then titrated in the way already described.

The following figures and ratios, the result of four consecutive titrations, made after I had determined the best conditions, serve to show that the method is fairly trustworthy, and sufficiently accurate for ordinary purposes:—

| Weight of lead taken. Grms. | Ratio between weight of lead and No. of c.c. used. |
|---|---|
| 0·1105 | 2188 |
| 0·1058 | 2186 |
| 0·1070 | 2189 |
| 0·1063 | 2183 |
| | 8746 |

Mean ratio .. .. .. .. .. 21865
Widest difference from mean .. +25 or −35

These results are quite within the errors due to the burette readings, and are, I think, fairly satisfactory, and seem to show that this method may be safely used for rapidly estimating small quantities of lead.

On adding the acetate to the neutral solution, basic salts usually separate, and the addition of the chloride causes a slight cloudiness as well. The long heating evidently converts these precipitates completely into chromate, and the result does not seem to be affected by the varying amounts of precipitate that may be formed.

The method might doubtless be used for estimating larger quantities of lead by adding a weighed quantity of pure bichromate of potash, heating, and then finishing the precipitation with the standard solution.

## ON A SOURCE OF ERROR IN EVAPORATING OVER SULPHURIC ACID.

By GEORGE STILLINGFLEET JOHNSON.

IN the CHEMICAL NEWS (vol. lxiii., p. 151) is published a paper which was read at the Chemical Section of the Franklin Institute, Jan. 20, 1891. The title of this paper—"Is Sulphuric Hydrate Volatile at the Ordinary Temperature of the Air?"—indicates that it deals with a question of the greatest importance to all chemists. After reading it, I at once set a number of experiments on foot with the object of throwing light upon the point at issue. As the results of these experiments are of some interest I have recorded them here.

Before entering upon a description of my own experiments, I will briefly summarise the observations and conclusions of the author of the paper mentioned above.

After keeping some pure iron in an ordinary desiccator over sulphuric acid (pure) for nine months, he found the metal coated with an anhydrous ferrous sulphate. The lid of the desiccator was kept tight by means of vaseline. From this observation the conclusion is drawn that sulphuric hydrate is volatile at the ordinary temperature of the air.

It happened that just before I read the above, a student in King's College Chemical Laboratory had been puzzled to account for reduction of a silver salt, which had been dried in an ordinary desiccator over sulphuric acid in a partial vacuum. I suggested that the reduction might be due to gases from the grease used to keep the receiver air-tight acting upon the sulphuric acid, and to avoid such action I recommended the addition of some chromic anhydride to the sulphuric acid. This was done, and the next sample of silver salt escaped reduction altogether.

It occurred to me, therefore, that reducing-gases from the vaseline might, in like manner, have been the cause of the formation of ferrous sulphate in the experiment quoted above; sulphur dioxide being generated and attacking the metal.

The method I adopted in examining this question was to take solutions of a compound stable in common air, but very easily deoxidised by reducing agents, and evaporate these solutions under varying circumstances, noting the results in each case. In order to accelerate matters the evaporations were generally carried on in a partial vacuum. The pump which I used (Fleuss's) gave a vacuum the residual tension in which was represented by one-fiftieth of an inch mercurial column.

My first experiments were made with potassium permanganate.

*Experiment* 1.—30 c.c. of a solution of potassium permanganate, saturated at 67° F. (19·5° C.), weighed 31·0601 grms. Evaporated in a vacuous desiccator, kept air-tight by grease, over sulphuric acid containing $CrO_3$ in solution. A mercury gauge left in the desiccator maintained a constant level throughout the experiment. The residue left in the dish weighed 1·7514 grms.; its weight remained constant at 100° C. Hence solubility of $K_2Mn_2O_8$ = 1 in 16·734 parts of water at 67° F.

*Experiment* 2.—The most perfect crystals were picked out from the residue from Experiment 1; their weight was 1·3306 grms. These crystals were re-dissolved in water and evaporated in precisely the same conditions as in Experiment 1. The weight of crystals left on evaporation was exactly the same as the weight taken, viz., 1·3306 grms.

From this it appears that potassium permanganate undergoes no decomposition when its aqueous solution is evaporated *in vacuo*.

*Experiment* 3.—30 c.c. of the same potassium permanganate solution as in Experiment 1 weighed (in a covered dish) 31·0570 grms. The dish was uncovered, and the solution was evaporated in a vacuous desiccator kept air-tight by grease which had been previously washed until quite free from acid reaction. To avoid spirting from the rapid evaporation, the exhaustion was stopped as soon as the tension was reduced to 1 inch of mercury. Fresh sulphuric acid was used for absorbing the water-vapour, but no $CrO_3$ was dissolved in it. The residue obtained weighed 1·7167 grms. This gives the solubility of permanganate of potassium 1 in 17·091 parts of water. This residue contained a brown deposit ($Mn_3O_4$), was deliquescent, and gave an alkaline solution in water. Hence every indication of *reduction* was obtained.

In all these experiments, the presence of metallic supports for the dishes, &c., was rigidly avoided. The vessels were placed on a ground-glass plate, covered with a glass receiver with ground welt, and glass tripods were used for supporting the upper dishes. The only possible source of the reducing agents which acted upon the permanganate was therefore the *grease* (mutton fat) used to keep the receiver air-tight.

On examining the sulphuric acid which had been used in the above experiment it showed evidence of reduction. 100 c.c. of the used acid decolourised 5·2 c.c. of a solution of potassium permanganate containing 0·2 grm. of $K_2Mn_2O_8$ in 500 c.c. 100 c.c. of the unused sulphuric acid (from the same bottle) decolourised only 1·9 c.c. of the same permanganate solution.

*Experiment* 4.—In this experiment a covered dish was again used, the glass lid overlapping and turned down at the edges, but, of course, not fitting air-tight. 20 c.c. of the same saturated permanganate solution was weighed in this dish (weight = 20·7725 grms.). The solution was evaporated *in vacuo, with the lid on*, over sulphuric acid with no $CrO_3$ dissolved in it, the apparatus being kept air-tight by grease, as before. The weight of dry permanganate crystals obtained was 1·790 grms. This gives the solubility of permanganate as 1 in 16·61 parts of water at 19·5° C. The crystals were perfectly pure, since the reducing gases had no access to them until the evaporation ceased. These crystals were now re-dissolved, and the solution evaporated with the lid off, spirting being carefully avoided by regulating the degree of exhaustion; other conditions the same as before. The weight of residue obtained was 1·1732 grms., and there was distinct evidence of reduction—brown deposit in the dish, &c.

*Experiment* 5.—A natural suggestion was to employ some material other than grease for keeping the desiccating apparatus air-tight. I am indebted to my friend and colleague, Mr Herbert Jackson, for preparing a substance which answers the purpose admirably in excluding air, and at the same time is free from the objection of yielding reducing vapours. The proportions of the ingredients are as follows:—

| | |
|---|---|
| Melted vaseline .. .. .. | 1½ fluid ozs. |
| Vulcanised indiarubber.. .. | ¾ oz. |
| Solid paraffin-wax .. .. .. | 1 drachm. |

These ingredients are heated together in a porcelain crucible until the greater part of the volatile matter is expelled. The product is a dark brown sticky mass, which does not alter in any way on being kept. 20 c.c. of the same permanganate solution (weight = 20·733 grms.) was evaporated in an open dish over sulphuric acid containing no $CrO_3$, but instead of grease the apparatus was kept air-tight by Mr. Jackson's lubricant. The weight of dry crystals was 1·1735 grms.; this gives the solubility of permanganate 1 in 16·66 parts of water. The crystals were pure.

The general conclusion from the above experiments is that—

1. Reduction of permanganate takes place during its evaporation over sulphuric acid in presence of vapours from common grease.

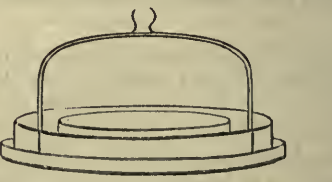
2. This reduction may be avoided by evaporating in a covered vessel, or by dissolving $CrO_3$ in the sulphuric acid, or by employing a substance which yields no reducing vapours instead of grease.

The determinations of the solubility of potassium permanganate at 19·5° C. agree well when precautions are taken to avoid reduction. Thus.—

| | |
|---|---|
| Experiment 1 .. .. .. | 1 in 16·734 |
| " 4 .. .. .. | 1 in 16·61 |
| " 5 .. .. .. | 1 in 16·66 |
| | 3)50·004 |
| Mean .. .. .. | 1 in 16·666 |

It will be observed that the figure indicating the greatest solubility was obtained from the experiment in which the dish was *covered* during the evaporation.

So far, my experiments have proved that a reducing atmosphere is produced by the interaction of vapours from fatty substances and sulphuric acid, and that the sulphuric acid itself suffers reduction in these circumstances (Experiment 3). The following experiments were conducted in a large desiccator constructed entirely of glass, the receiver of which has a glass ring both inside and outside it.



By pouring mercury into the space between the outer ring and the receiver, we can ensure the complete exclusion of the outer air. The exhaustion is effected by means of a glass tube in the centre of the glass plate. The dishes, &c., were supported on glass tripods.

*Experiment* 6.—In this experiment I tested incidentally the veracity of a statement which has been recently made to the effect that evaporation takes place more rapidly when the vessel containing the absorbent for the vapour is above the evaporating liquid. Three glass dishes of equal diameter and capacity were employed. The lowest and the uppermost dish each contained 200 c.c. of a solution of $CrO_3$ in sulphuric acid; the middle dish contained a cold saturated solution of potassium hydroxide, perfectly free from sulphur compounds. The desiccator was then exhausted until a mercury gauge within it showed one-fiftieth of an inch of gaseous tension. This exhaustion was maintained for four months. The opaque residue in the middle dish was then dissolved, acidulated with pure hydrochloric acid, and mixed with a solution of barium chloride. No trace of barium sulphate was formed. The volume of liquid in the upper and lower dishes was exactly the same, viz., 250 c.c., and the specific gravity of the two liquids was exactly equal, viz., 1·725. It appears, therefore, that in a good vacuum the position of the absorbent—whether above or below the evaporating liquid—is a matter of no importance. We have also a negative result as regards volatilisation of sulphuric acid.

There is, however, an obvious objection to the above experiment as a test of the possible volatilisation of sulphuric acid, inasmuch as the dilution of the acid by the condensed water from the potash solution might have hindered volatilisation. Therefore the following experiment was performed.

*Experiment* 7.—The same large desiccator was employed. Mr. Jackson's lubricant was used to keep it air-tight. Sulphuric acid containing $CrO_3$ in solution was used, and above it was placed a porcelain dish containing the liquid alloy of potassium and sodium. The vacuum was made as before, on April 25, 1893. The air was re-admitted on July 15, 1893. The metal still in the dish was oxidised and hydrated by leaving it under a glass shade with a dish of water near it. The contents of the dish were dissolved, acidulated with HCl, and treated with barium chloride. Not a trace of $BaSO_4$ was formed.

*Experiment* 8.—In this experiment common grease was used to keep the desiccator air-tight. Sulphuric acid without chromic anhydride was employed. The sodium and potassium alloy was placed as before, and the exhaustion was maintained for a month. On dissolving and acidulating the sodium and potassium compounds and adding barium chloride, precipitation took place, and I collected and weighed 17 m.grms. of barium sulphate.

My conclusion is that sulphuric acid is certainly not volatile at ordinary temperatures, even in a good vacuum, but that it is liable to vitiate the results of our experiments if exposed to reducing vapours.

Chemical Laboratory, King's College,
London, October 14, 1893.

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## SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.

By Prof. Dr. FRESENIUS.

I am now in a position to recommend trustworthy methods for the separation of barium, strontium, and calcium, when the three alkaline earths are jointly present. I will first speak of a process which appears particularly suitable for the recognition of the three alkaline earths when they exist together without the aid of spectroscopic analysis. It is a combination of known methods which have been mostly described in my former memoirs. I can recommend the method as simple in execution, and as successful even when only a very small quantity of barium, strontium, or calcium is present along with larger quantities of each of the other alkaline earths, as I have satisfied myself by repeated experiments.

In qualitative analysis, if we separate baryta, strontia, and lime from magnesia, we obtain the three former as carbonates. After washing we dissolve them in dilute nitric acid, evaporate the solution to dryness in a small porcelain capsule, heat it for ten to fifteen minutes very strongly on an iron plate (the temperature may be safely allowed to rise to 180°) until the residue no longer smells of nitric acid, and until a cold glass plate—placed as a cover over the capsule for a few seconds—is no longer bedewed with water-drops. The contents of the capsule when cold are immediately ground up, first dry, and then with the addition of 5 to 10 c.c. of a mixture of equal vols. of ether and absolute alcohol. After a few minutes the solution is filtered off, and the residue washed four times with small quantities of the mixture of ether and alcohol. We have now in the residue the barium and strontium nitrates, to which small portions of calcium nitrate may still adhere; and in the filtrate the calcium nitrate in which, without due care in working, demonstrable traces of strontium nitrate may be present.

To the ether-alcoholic solution there are now added two drops of dilute sulphuric acid. If there appears any appreciable precipitate it can only be calcium sulphate, and there can be no occasion to test further for calcium. If the precipitate is very slight it may be due to traces of strontium which have possibly passed into the ether-alcoholic solution. In this case we mix the solution with 4 c.c. of water, evaporate away the ether and alcohol, add a few drops of ammonia and about 1 grm. of ammonium sulphate. heat to ebullition, filter through a small filter, add to the filtrate a drop of acetic acid so that it just reddens litmus-paper, and then a few drops of ammonium oxalate. If lime is present there appears at once (or in case of very small quantities after standing) a precipitate of calcium oxalate. It cannot be mistaken for the minute quantities of strontia possibly present, because the traces of strontium sulphate which dissolve in a concentrated solution of ammonium sulphate are not precipitated by ammonium oxalate in presence of a trace of free acetic acid.

The barium and strontium nitrates are dissolved with heat in about 100 c.c. of water, filtered if necessary, acidulated with 3 to 4 drops of acetic acid, heated to ebullition, gradually adding neutral potassium chromate until the solution has a yellow colour, and allowed to boil again. If the odour of acetic acid is still felt we add a little more potassium chromate. If barium is present there appears at once (or in case of very small quantities after a short time) a light yellow precipitate. The liquid is allowed to stand for an hour, filtered, and to a portion of the filtrate there is added ammonia, and then ammonium carbonate. If there appears any appreciable precipitate it can be nothing but strontium carbonate, and there is then no need to test further for strontium. If there is no precipitate, or merely one extremely slight, we add to the bulk of the filtrate one or two drops of nitric acid, concentrate to from 10 to 20 c.c., and add then ammonia and ammonium carbonate. If still no precipitate is formed, strontium is not present; but if a slight precipitate appears it may be strontia, or possibly traces of lime. The small precipitate is filtered off, washed, dissolved in a few drops of dilute hydrochloric acid, and the solution is evaporated to dryness. The slight residue of the neutral chloride, or neutral chlorides, is dissolved in 1 or 2 c.c. of a mixture of 3 parts of water and 1 part of alcohol, which is kept in readiness; one drop of the solution of yellow potassium chromate is added, and the liquid is heated to incipient ebullition. If strontium is present it separates out at once (or after standing in heat for a short time) as a finely pulverulent yellow precipitate of strontium chromate.

For the quantitative separation of barium, strontium, and calcium, the following considerations are decisive:—

1. For the accurate separation of barium, strontium, and calcium, only two methods have been found quite suitable,—*i.e.*, the separation of the barium as chromate or as silico-fluoride.

2. The separation of strontium from calcium succeeds only by treating the nitrates with ether-alcohol. This

treatment is also suitable for separating barium from calcium.

3. A liquid in which hydrosilico-fluoric acid is present along with strontium and calcium is not well suited for determining the two alkaline earths, since they can then be thrown down only as sulphates, consequently in a state in which they are not directly separable.

To effect the purpose the following proceedings are essential:—

(*a*) Barium and strontium are separated from calcium by treating the nitrates with ether alcohol, and from the solution of the former the barium is separated as chromate.

(*b*) The barium is separated in the first place as chromate. The strontium and calcium are converted first into carbonates and then into nitrates which are separated by ether alcohol.

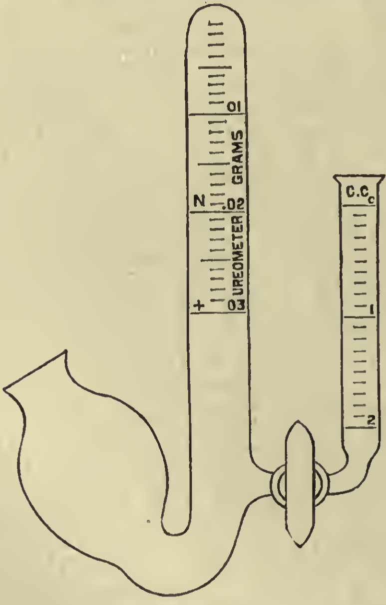
Both these methods yield satisfactory results, and the one or the other will be found preferable according to the circumstances.—*Zeit. fur Anal. Chemie*, xxxii., p. 312.

## IMPROVED UREOMETER.

By Prof. J. I. D. HINDS,
Cumberland University, Lebanon, Tennessee, U.S.A.

In using the ureometer designed by Professor Doremus I have found two sources of considerable error. In the first place it is impossible to run in from the pipette exactly 1 c.c. of the urine. In the second place some bubbles of nitrogen almost invariably escape at the bulb.

To avoid these errors I have devised the apparatus shown in the accompanying figure. A tube graduated to tenths of c.c. is attached on the side opposite the bulb, and the two tubes are connected by a stop-cock. The instrument is filled with the test-fluid in the usual way, and then the small tube is filled with the urine. Exactly 1 c.c. is allowed to run in through the stop-cock, and then the nitrogen evolved is measured in the larger tube. The instrument gives as great accuracy as can be attained with the small quantities dealt with.



(Half natural size).

The hole in the stop-cock should be filled with the urine. This can be done by running in a few drops of the urine before filling with the test-fluid. The instrument is conveniently held with the left hand, while the stop-cock is being operated with the right.

### ON THE
## ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Continued from p. 203).

### Naphthol β ($C_{10}H_8O$).

A solution was prepared containing 2 grms. naphthol and 3 grms. caustic soda in 300 c.c. of water. 20 c.c. of this solution was diluted to about 300 c.c., and the whole heated to 60° C., the iodine solution being then run in to large excess. The solution soon became opalescent, and after cooling a little the bulk of the product fell out as a precipitate. The mixture was then acidified in order to practically complete the precipitation. This process was repeated until a sufficient quantity was obtained.

The precipitate, when washed and dried, was of a dark greenish brown colour and of pulverulent character; when treated with cold alcohol, only a very small portion dissolved out. It was then treated with boiling alcohol, which dissolved out the greater portion of the remainder. The alcohol-soluble portion, when recovered, was of a shiny brittle character, and appeared black; but when powdered was of a dark brown colour. This was air-dried and then taken for analyses; it melted readily with decomposition.

Total iodine of the boiling alcohol-soluble portion:—
Quantity taken =0·1297 grm.
Silver iodide found=0·0696 ,, =28·99 p.c. iodine.

Combustion of same:—
Quantity taken =0·1282 grm.
Water found =0·0419 ,, = 3·63 p.c. hydrogen.
Carbon dioxide found =0·2581 ,, =54·80 ,, carbon.
By difference .. .. =12·58 ,, oxygen.

The presence of water being suspected, the remainder was dried for fourteen days, and the iodine re-estimated.

Quantity taken =0·1899 grm.
Silver iodide found=0·1032 ,, =29·36 p.c. iodine.

The remainder of the precipitate from the boiling alcohol treatment was dissolved out with chloroform and recovered. It was of a black-brown colour, and melted with decomposition.

Total iodine of the alcohol-insoluble portion:—
Quantity taken =0·1089 grm.
Silver iodide found=0·0312 ,, =15·48 p.c. iodine.

Combustion of same:—
Quantity taken =0·0978 grm.
Water found =0·0387 ,, = 4·39 p.c. hydrogen.
Carbon dioxide found =0·2145 ,, =59·81 ,, carbon.
By difference .. .. =20·32 ,, oxygen.

As no satisfactory formulæ could be derived from the above analyses, a new batch was prepared under like conditions. The precipitate obtained was of precisely the same appearance. The whole precipitate was heated in sealed tube with copper and water at a temperature of about 140° C. for twelve hours. The product was dried and treated with cold alcohol, which dissolved out a small quantity. The remainder was then treated with ether and the soluble portion recovered. This was of a light brownish colour, and melted readily with decomposition. It gave the following results on analyses:—

Total iodine of the alcohol-insoluble portion, soluble in ether:—
Quantity taken =0·1043 grm.
Silver iodide found=0·0103 „ =5·33 p.c. iodine.

Combustion of same:—
Quantity taken =0·0938 grm.
Water found =0·0350 „ = 4·14 p.c. hydrogen.
Carbon dioxide found =0·2562 „ =74·49 „ carbon.
By difference .. .. =16·04 „ oxygen.

The remainder of precipitate was then treated with chloroform, the soluble portion recovered and submitted to analyses. Colour of a dark greenish brown.

Total iodine of the alcohol-ether-insoluble portion:—
Quantity taken =0·1306 grm.
Silver iodide found=0·0506 „ =20·93 p.c. iodine.

Combustion of same:—
Quantity taken =0·0918 grm.
Water found =0·0292 „ = 3·53 p.c. hydrogen.
Carbon dioxide found =0·2436 „ =72·37 „ carbon.
By difference .. .. = 3·17 „ oxygen.

The naphthol, originally taken as the basis of those preparations, was again very slowly sublimed over a sulphuric acid bath, and the sublimate used for the preparation of another batch. The precipitate obtained was quite similar in appearance to those already examined.

This precipitate was treated with cold alcohol and the soluble portion recovered. This was re-dissolved in alcohol, and the alcoholic solution treated with successive portions of water until the dissolved substance was almost completely precipitated; the precipitate was then filtered out, washed, and dried. It was of a light yellowish brown colour and melted readily.

Total iodine of the alcohol-soluble portion (precipitated):—
Quantity taken =0·1728 grm.
Silver iodide found=0·0311 „ =9·73 p.c. iodine.

Combustion of same:—
Quantity taken =0·1066 grm.
Water found =0·0421 „ = 4·38 p.c. hydrogen.
Carbon dioxide found =0·2801 „ =71·65 „ carbon.
By difference .. .. =14·24 „ oxygen.

The remainder of the precipitate was treated with ether, to which it yielded the greatest part. The soluble portion was recovered, dried, powdered, and heated for about twelve hours in air oven at a temperature of about 100° C. The colour and physical properties were quite similar to those of the alcohol-soluble portion.

Total iodine of the alcohol-insoluble portion:—
Quantity taken =0·1235 grm.
Silver iodide found=0·0239 „ =10·46 p.c. iodine.

Combustion of same:—
Quantity taken =0·0699 grm.
Water found =0·0235 „ = 3·73 p.c. hydrogen.
Carbon dioxide found =0·1866 „ =72·79 „ carbon.
By difference .. .. =13·02 „ oxygen.

The remainder of precipitate was treated with cold chloroform, which dissolved out a small quantity. The remainder was then treated with boiling chloroform, which dissolved out a further portion. This was recovered, and when dry presented a dull, dark, greenish brown appearance. It was heated in the air-oven at about 100° C. for two days, at the end of which time it had assumed a beautiful lustrous green colour, somewhat dichroic and almost crystalline. It was then submitted to analyses.

Total iodine of the alcohol-ether-chloroform-insoluble portion (soluble in boiling chloroform):—
Quantity taken =0·0759 grm.
Silver iodide found=0·0144 „ =10·25 p.c. iodine.

Combustion of same:—
Quantity taken =0·0690 grm.
Water found =0·0222 „ = 3·57 p.c. hydrogen.
Carbon dioxide found =0·1737 „ =68·65 „ carbon.
By difference .. .. =17·53 „ oxygen.

"Encluded" iodine being still further suspected, a weighed quantity of the same was heated to about 150° C., when a further small portion of iodine was given off, which may be stated roundly as 1 per cent.

The remainder of the precipitate from the boiling chloroform treatment was dried and heated on an acid bath at a temperature of about 150° C. until it had parted with all its "encluded" iodine. (Iodine lost by heating 1·76 per cent). It was then taken for analyses.

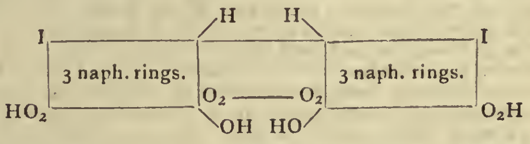
Total iodine:—
Quantity taken =0·1358 grm.
Silver iodide found=0·0568 „ =22·59 p.c. iodine.

Combustion of same:—
Quantity taken =0·0808 grm.
Water found =0·0214 „ = 2·94 p.c. hydrogen.
Carbon dioxide found =0·1646 „ =55·55 „ carbon.
Ash .. .. .. .. .. .. = 5·40 „

Allowing for ash in above analyses we have—

| | |
|---|---|
| Carbon .. .. .. .. .. | =58·72 |
| Hydrogen.. .. .. .. .. | = 3·11 |
| Iodine .. .. .. .. .. | =23·88 |
| Oxygen .. .. .. .. .. | =14·29 |

This portion, therefore, may possibly be represented by the formula $C_{26}H_{15}IO_5$. Following up this result analogously one would be compelled to double this formula and assume a chain of rings made up of three naphthalene rings, with elimination of four carbon atoms, and then assume condensation of such molecules, thus—



To assume such without the most convincing confirmatory evidence would be altogether out of the question. At the same time, if one naphthol molecule substituted an atom of iodine for hydrogen, why not all? As an alternative the following structure might be assumed, which will explain itself:—

Admitting this it would appear that β-naphthol takes up no iodine under the conditions. This, and also the portions dissolved out by chloroform, is soluble in strong sulphuric acid, with beautiful violet colour, a brownish precipitate falling out on dilution with water. The portions dissolved out by alcohol and ether are not affected.

Messinger and Vortmann in their paper remark that the analyses did not give good results. The iodine percentage reported by them for the total precipitate obtained from $\beta$-naphthol was 40·7, whilst they point out that naphthol iodide requires 47 per cent. They give the colour of the precipitate as yellowish green, but this is only the case when a meagre excess of iodine is added. It is worthy of remark that the highest iodine percentage obtained by me was from a precipitate prepared from the more impure sample. However, conditions might possibly be set up which would yield compounds containing an equivalent of iodine to each original molecule, as would appear to have been obtained by Messinger and Vortman.

(To be continued.)

### ON THE
# ESTIMATION OF CHLORATES AND NITRATES, AND OF NITRITES AND NITRATES IN ONE OPERATION.*

By **CHARLOTTE F. ROBERTS.**

A recent paper by Gooch and Gruener (*Am. Journ. Sci.*, xliv., 117) has shown that nitrates may be estimated most accurately by treatment with manganese chloride, the chlorine thus liberated being collected in potassium iodide, and the amount of iodine set free determined by titration with sodium thiosulphate. In a late number of the *American Journal of Science* (xlvi., 126, August, 1893), I have shown that good results are also obtained by treatment of the nitrate with ferrous chloride, and collecting and measuring the nitric oxide evolved over sodium hydroxide with the apparatus described and pictured in that article.

This apparatus consists essentially of a small retort fitted with a hollow ground-glass stopper prolonged beneath in a tube, and joined above with two branching tubes through one of which carbon dioxide may enter, and the other of which is attached to a funnel-tube with stopcock, through which liquids may be introduced without admitting air. The retort is connected with a small condenser, which in turn is attached to a Will and Varrentrapp tube containing potassium iodide, and this with a Hempel's burette containing a strong solution of sodium hydroxide. In the experiments described, the potassium nitrate was introduced into the retort, carbon dioxide passed through until the air was completely driven out, and then ferrous chloride added through the funnel-tube. After heating, and passing a current of carbon dioxide through the apparatus, the volume of gas unabsorbed by sodium hydroxide was measured at the observed temperature and pressure, and from this the weight of potassium nitrate was calculated. This is merely a special form of a very common method of estimating nitrates, but the apparatus is in a form which can be conveniently handled and which readily adapts itself to other uses beside the simple determination of nitrates. In a mixture of chloric and nitric acids, for example, it becomes possible by a combination of the two above-named methods for estimating nitrates, and the use of the apparatus described, to determine in one operation the amounts of each present. A method for the determination of chlorates which has long been in common use consists in treatment with hydrochloric acid, the liberated chlorine being conducted into potassium iodide, and the iodine set free determined by titration by sodium thiosulphate. This method is entirely analogous to the first-mentioned method of determining nitrates, the only difference being that in the latter case a solution of manganous chloride in hydrochloric acid is used instead of the acid alone. In case of the nitrate, however, there is a second product, nitric oxide, which may be collected and measured. It would then seem possible, with the use of the apparatus heretofore described, to treat a mixture of a chlorate and nitrate with manganous chloride, pass the resulting gases through potassium iodide, and then into the Hempel's burette. The amount of nitric oxide will give at once the amount of nitrate present. The iodine liberated will give the total chlorine set free by the reduction of the nitrate and chlorate. After that which is due to the nitrate determined has been deducted, we have an exact measure of the chlorate present.

To verify these presumptions, a few preliminary experiments were first made with potassium chlorate alone. In these, and all of the following experiments, great care was taken that the escaping gases should only come in contact with glass. Between the condenser and Hempel's burette were two Will and Varrentrapp tubes sealed together and containing potassium iodide, and generally a Geissler bulb containing potassium iodide was also added to make sure that no chlorine escaped absorption. The potassium chlorate was weighed out and introduced into the retort, air driven out by carbon dioxide, and then manganous chloride added through the funnel-tube. The liquid became dark at once, and a short heating sufficed to restore it to its original clear light green colour. When this was accomplished, a current of carbon dioxide was passed through the apparatus, the bulbed tubes were disconnected, and their contents titrated with sodium thiosulphate. The following results were obtained from five trials:—

| | Wt. $KClO_3$ taken. | Wt. $KClO_3$ found. | Difference. |
|---|---|---|---|
| 1. | 0·1000 | 0·0990 | 0·0010 |
| 2. | 0·1000 | 0·0995 | 0·0005 |
| 3. | 0·0500 | 0·0484 | 0·0016 |
| 4. | 0·0500 | 0·0498 | 0·0002 |
| 5. | 0·0500 | 0·0496 | 0·0004 |

Working in the same way with a mixture of potassium chlorate and potassium nitrate, and estimating the amount of nitrate first from the nitric oxide produced, the following results were obtained:—

| | | Weights taken. | Weights found. | Difference. |
|---|---|---|---|---|
| 1. | Potassium chlorate.. | 0·0500 | 0·0515 | 0·0015 |
| | Potassium nitrate .. | 0 0500 | 0·0494 | 0·0006 |
| 2. | Potassium chlorate.. | 0·0500 | 0·0508 | 0·0008 |
| | Potassium nitrate .. | 0·0500 | 0·0493 | 0·0007 |
| 3. | Potassium chlorate.. | 0·1000 | 0·0987 | 0·0013 |
| | Potassium nitrate .. | 0·1000 | 0·0995 | 0·0005 |
| 4. | Potassium chlorate.. | 0·1000 | 0·1007 | 0·0007 |
| | Potassium nitrate .. | 0·1000 | 0·0980 | 0·0020 |
| 5. | Potassium chlorate.. | 0·0300 | 0·0305 | 0·0005 |
| | Potassium nitrate .. | 0·1000 | 0·0990 | 0·0010 |
| 6. | Potassium chlorate.. | 0·1000 | 0·1006 | 0·0006 |
| | Potassium nitrate .. | 0·0300 | 0·0293 | 0 0007 |

The method is simple, rapid, and easy, and sufficiently accurate for most analytical work. One objection that may be urged against it is that any error in the determination of the nitric acid involves a corresponding error in the amount of chloric acid, but the above results show that such errors will be quite small if the experiment is conducted with proper precautions.

It also appeared probable that a nitrate and nitrite could be estimated at one operation in a somewhat similar manner. By the action of manganous chloride on a mixture of nitric and nitrous acids, nitric oxide and iodine would be set free from each. Representing the weight of nitric oxide found by *a*, and the weight of iodine found by *b*, and letting *x* equal the amount of nitric acid operated upon, and *y* the amount of nitrous acid,—

$$\frac{30}{63}x + \frac{30}{47}y = a, \text{ and}$$

$$\frac{379·5}{63}x + \frac{126·5}{47}y = b;$$

whence,—

$$x = 0·249\,b - 1·049\,a$$
$$y = 2·35\,a - 0·186\,b$$

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* *American Journal of Science*, xlvi., Sept., 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

In the attempt to verify these formulæ by experiment, a little difficulty was found in getting a pure and stable nitrite upon which to operate. Some silver nitrite was prepared by precipitation from potassium nitrite and silver nitrate. This was washed well and dried as thoroughly as possible over sulphuric acid in the dark. Weighed portions were put in the retort, and after the air was expelled, manganous chloride was added. The amount of silver nitrate was then estimated from the iodine set free in the bulbed tubes, and also from the nitric oxide left in the Hempel burette. The results varied from one another by 4 or 5 per cent on different portions, but a few trials were sufficient to indicate that the trouble lay in the silver nitrite, and not in the process itself. The percentage of purity as obtained from several trials by ignition was 98·4 per cent. The average of ten trials estimating from nitric oxide gave 98·1 per cent, and from the liberated iodine 98·7 per cent. This was uniformity enough to indicate that the method of work was trustworthy, although there was apparent such a lack of homogeneity in the silver nitrite as to make it impossible to use it in testing the value of the formula given above.

To obviate this difficulty more silver nitrate was precipitated, well washed, dissolved in warm water, and a solution of sodium chloride added. The silver chloride was then filtered off, and the resulting solution of sodium nitrite was used in the following experiments. To determine the strength of this solution 10 or 15 c.c. were drawn off from a burette, and the nitrite estimated with potassium permanganate according to the method of Kinnicutt and Nef (*Ann. Chem. Journ.*, v., 388). At the same time similar amounts were introduced into the retort with manganous chloride, and the nitrite estimated both from the liberated iodine and the nitric oxide formed. It was found that the air must be thoroughly driven out of the apparatus before the nitrite was introduced, as the carbon dioxide, passing over the solution, decomposed it with liberation of nitric oxide, which, in presence of air, gave an excess of free iodine, and at the same time a little gas was lost. Accordingly carbon dioxide was first passed through the apparatus for some time, then the nitrite was introduced through the funnel-tube and rinsed in with a little water, followed by the manganous chloride solution, care being taken that the water should not exceed one-third of the total volume of the liquid, according to the precaution to be shown necessary by Gooch and Gruener. Working in this way with the solution of sodium nitrite, the following results were obtained :—

| | Vol. taken | Weight reckoned from $KMnO_4$. | Wt. reckoned from NO. | Wt. reckoned from Iodine. |
|---|---|---|---|---|
| | C.m. | Grm. | Grm. | Grm. |
| 1. | 10 | 0·0463 | 0·0456 | 0·0450 |
| 2. | 10 | 0·0460 | 0·0460 | 0·0470 |
| 3. | 15 | 0·0704 | 0·0708 | 0·0722 |
| 4. | 15 | 0·0690 | 0·0712 | 0·0750 |
| 5. | 15 | 0·0701 | 0·0704 | 0·0722 |
| 6. | 15 | 0·0688 | 0·0696 | 0·0695 |
| 7. | 15 | 0·0706 | | |
| 8. | 15 | 0·0712 | | |

It will be seen that the results reckoned from the iodine are in general larger than those obtained by either of the other methods. This is what might be expected on account of the difficulty of completely removing air from the apparatus and solutions employed, and such air would naturally cause an excess of iodine. In No. 4 especially it will be noticed that we have an abnormally large amount of iodine set free, and this may undoubtedly be attributed to air, since it was observed that the current of carbon dioxide was rather sluggish at the time of that experiment.

The average of the above-recorded experiments would give as the value of 15 c.c., from the method of Kinnicutt and Nef, 0·0697 grm., from the nitric oxide 0·0699 grm., and from the iodine 0·0711 grm. If we assume that the mean weight per 15 c.c. is represented by the average of these three modes of determination, we obtain 0·0702 grm., and that is the number which is used in the following derermination to represent the weight of sodium nitrite in 15 c.c. of the solution. The following experiments were made in the same way as the preceding, except that potassium nitrate was introduced in the dry state before the air was driven out of the apparatus, and the results were calculated from the formula given above :—

| | | Weights taken. | Weights found. | Difference. |
|---|---|---|---|---|
| 1. | Sodium nitrite .. .. | 0·0702 | 0·0718 | 0·0016 |
| | Potassium nitrate .. | 0·1000 | 0·1000 | 0·0000 |
| 2. | Sodium nitrite .. .. | 0·0702 | 0·0712 | 0·0012 |
| | Potassium nitrate .. | 0·1000 | 0·0999 | 0·0001 |
| 3. | Sodium nitrite .. .. | 0·0702 | 0·0710 | 0·0008 |
| | Potassium nitrate .. | 0·1000 | 0·1004 | 0·0004 |
| 4. | Sodium nitrite .. .. | 0·0702 | 0·0698 | 0·0004 |
| | Potassium nitrate .. | 0·1000 | 0·1012 | 0·0012 |
| 5. | Sodium nitrite .. .. | 0·0468 | 0·0453 | 0·0013 |
| | Potassium nitrate .. | 0·1000 | 0·0994 | 0·0006 |
| 6. | Sodium nitrite .. .. | 0·0468 | 0·0444 | 0·0024 |
| | Potassium nitrate .. | 0·0500 | 0·0519 | 0·0013 |

Though the process is one in which the most perfect accuracy cannot be assured in all cases, the above results show that it is capable of giving fairly accurate results, sufficient for many analytical purposes. It seems to be especially well adapted to the estimation of the commercial alkali nitrites, the whole determination being made on one portion and by one operation, instead of on two different portions.

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## ON ERBIA.*

By GERHARD KRÜSS.

(Concluded from p. 202).

We must further report on the elaboration of the third portion of the erbia earths received from L. F. Nilson. This earth may be called

*Erbia Material No.* 10 ($\overset{\text{II}}{R} = 166{\cdot}9$),

This material was in the alcoholic solution of its chloride submitted to fractionated precipitation with an alcoholic solution of aniline.

*Series* 20.

Weak bases ⟵.

" Aniline precipitates."

$$\underbrace{\overset{1}{167{\cdot}7}\quad\overset{2}{168{\cdot}0}\quad\overset{3}{—}\quad\overset{4}{167{\cdot}2}}_{\alpha}\quad\underbrace{\overset{5}{—}\quad\overset{6}{168{\cdot}5}}_{\beta}\quad\underbrace{\overset{7}{—}\quad\overset{8}{165{\cdot}6}}_{\gamma}$$

⟶ Strong bases.

" Aniline precipitates."

$$\underbrace{\overset{9}{167{\cdot}3}\quad\overset{10}{168{\cdot}7}\quad\overset{11}{167{\cdot}3}\quad\overset{12}{—}}_{\delta}\qquad\underbrace{\overset{13\ \text{(Residue).}}{166{\cdot}5}}_{\varepsilon}$$

Mutually adjacent fractions of this series were systematically united as the materials $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon$, as shown by the brackets placed underneath Series 20, and from $\alpha$ a solution with aniline hydrochlorate was added to $\beta$, and finally one from $\varepsilon$ to the fraction 13. In an analogous manner the least basic portions of an earth were carried over into the fraction to the left in Series 20. Lastly, the material $\alpha$ was resolved into two portions, as—

---

* *Zeitschrift fur Anorganische Chemie.*

*Series 21.*

Weak bases ←—.

| α | | β |
|---|---|---|
| 1<br>Not dissolved | 2<br>Dissolved | |
| 168·8 | 167·7 | 167·2 |

—→ Strong bases.

| γ | δ | ε |
|---|---|---|
| 164·3 | 167·0 | 164·7 |

Between $\delta$ and $\epsilon$ there was an intermediate fraction $\delta/\epsilon$ obtained in the manner indicated in Series 19, fraction 6/7 and 7/8 in the same manner subsequently between $\gamma$ and $\delta$ and between $\beta$ and $\gamma$. At the same time the series of fractions No. 21 was worked up from side to side, and then inversely by aniline solutions and precipitations, and the $\alpha$ material obtained was resolved into several sub-fractions by treatment with aniline hydrochlorate.

*Series 22.*

Weak bases ←—.

| α | | | |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| 172·4 | 168·5 | — | 167·4 |

—→ Strong bases.

| β | β/γ | γ | γ/δ | δ | δ/ε | ε |
|---|---|---|---|---|---|---|
| 168·4 | 168·7 | 166·9 | — | 166·8 | 165·4 | 166·6 |

The erbia material No. 10 ($\overset{\text{III}}{R}=166{\cdot}9$), which possessed in the most distinguished manner the attributes ascribed to erbia, was resolved according to Series 22 into portions the analyses of which showed from fraction to fraction undulations in the value of $\overset{\text{III}}{R}$ and behaved like the larger erbia material (Nilson's) No. 9 corresponding to Series 19.

The above results may be associated as follows:—

If we resolve erbiferous yttria earths by fractionated, partial decompositions of the nitrates in heat, and further by the action of aniline or aniline hydrochlorate, and always consider as erbia materials those fractions which, according to gravimetric and spectroscopic analysis, should contain an erbium with $\overset{\text{III}}{Er}=166$—$168$, and display absorption spectrum lines at $\lambda=654{\cdot}7$ and $\lambda=523{\cdot}1$, we arrive in fact at an apparently unitary oxide, with about the equivalent which P. T. Cleve found for erbia. We arrive at the same confirmation of Cleve's researches if we resolve erbiferous yttria earths into a great number of fractions by the decomposition of the nitrates by heat alone. The erbia earths prepared in this manner by L. F. Nilson were excellent types of erbia earth.

But if by the above methods all the ytterbia, holmia, terbia, and yttria are eliminated from the erbia earth, and the value found for $\overset{\text{III}}{R}$ in determining the equivalents of the fractions has become almost constant (absolute constancy of the $\overset{\text{III}}{R}$ values was never found attainable in a large number of successive fractions), erbia is now found—perhaps by the very removal of the kindred earths—to have lost its relatively great stability and proves to be complex. Erbia can be resolved by treatment with aniline hydrochlorate into earths with different equivalents, so that we are not justified in regarding erbia as a peculiar oxide, $Er_2O_3$.

I shall endeavour to discuss the question of what erbia consists after the publication in early parts of this journal of two researches simultaneously conducted on holmia and terbia.

I must here express my thanks to my former assistant, Dr. Karl Hofmann, for his most valuable aid in conducting the above investigation.

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*Ordinary Meeting, October 27th, 1893.*

Prof. J. Perry, F.R.S., Vice-President, in the Chair.

Mr. E. C. Rimington read a paper "*On the Behaviour of an Air-core Transformer when the Frequency is below a certain Critical Value.*"

Taking the ordinary differential equations for two circuits having self and mutual induction, and assuming sinusoidal E.M.F.'s and constant coefficients, the author shows that although the difference of phase between the primary P.D. and primary current is always diminished on closing the secondary circuit, yet, under certain circumstances, this closing increases the impedance of the primary. With constant P.D., this means that closing the secondary decreases the primary current—a phenomenon not usually observed. The critical conditions necessary for increased impedance are fully worked out in the paper, as well as those under which this increase becomes a maximum. In the case of two identical coils with no magnetic leakage, the critical value of $\alpha$ ($\alpha=\frac{pL}{r}$ where $p=2\pi$ times the frequency, L the inductance of the primary, and $r$ its resistance) is $\sqrt{2}$, whilst that to give maximum impedance is $\frac{1}{\sqrt{2}}$. The maximum increase possible is 15¼ per cent. The corresponding values are given for various amounts of magnetic leakage in tabular form, and curves were exhibited at the meeting showing how the impedance, current, power, and magnetising effect vary for different values of $\alpha$.

To test his conclusions, the author made experiments on two coils close together; the observed increase in impedance amounted to 3·2 per cent.

In addition to analytical investigation, the subject is treated geometrically at considerable length.

Prof. Minchin showed that the impedances might be represented by two hyperbolas, having $p$ as abscissæ and the squares of the impedance as ordinates. These could be readily constructed from the data given. A line representing the primary inductance, drawn on the same diagram, intersects one hyperbola, showing that the impedance has always a maximum value. By a simple construction the phase angle between the primary and secondary currents could be determined for any given conditions.

Dr. Sumpner observed that increased impedance on closing the secondary necessarily meant a decrease in the lag of the primary current behind the primary P.D.

Mr. Blakesley was pleased to see the geometrical method of such service, and thought it much simpler than the analytical one. The reason why increased impedance on closing the secondary of ordinary transformers had not been noticed, was because their lag angles were very large. In a figure published some years ago to represent the actions of transformers, the angles he had chosen were such as would make the primary impedance increase on closing the secondary. Giving an expression connecting the primary currents on open and closed secondaty respectively, he now showed that to get increased impedance the sum of the lag-angles in primary and secondary must exceed 90°. To get large power in the secondary, the primary lag should be nearly 90° and the secondary about 45°. He also pointed out that some of the figures in the paper might be simplified considerably.

Prof. Perry said he had long had the impression that if a sufficiently small current were taken from the secondary, increased impedance would be observable in all cases, and he quoted some numbers he had given in the *Phil. Mag.* for 1891, showing a decided increase.

Mr. **Rimington**, in reply, said he was not aware that the effect he had now brought forward had been observed previously. The result was completely worked out analytically before using geometrical methods.

Mr. W. B. **Croft**, M.A., showed two Lecture-room Experiments. One, on "*The Rings and Brushes in Crystals*," was performed by very simple apparatus in two ways. In the first a bundle of glass plates was used as polariser, and a Nicol prism as analyser. When a Nicol could not be conveniently obtained, a glass plate could be used as a reflecting analyser. For a convergent system two glass card-counters were used, the crystal being placed between them. Very good results were produced by this simple apparatus.

In the second arrangement the crystal was placed on the eye-piece of a microscope (whose objective was removed), and covered by a tourmaline. On reflecting light up the tube by means of a piece of glass held at the proper angle, excellent results were obtained.

Another experiment, on "*Electric Radiation in Copper Filings*," was similar to those described by Dr. Dawson Turner at the Edinburgh Meeting of the British Association. A battery, galvanometer, and glass tube containing copper filings were joined in series. Under ordinary circumstances no current passed, but immediately an electric spark was produced by an electric machine many feet away, the galvanometer was violently deflected, and remained so until the tube was tapped. On trying different materials, aluminium and copper seemed about equal, but iron not so good. Carbon allowed the current to pass always.

Prof. **Minchin** said the phenomena were strikingly like those exhibited by his "impulsion cells," for the moment a spark passed, even at a distance of 130 feet, they became sensitive to light. Very minute sparks were capable of producing the change, but by adding capacity to the sparking circuit the effect could be greatly modified. Replying to a question from Mr. Rimington, he said the change was due to electro-magnetic vibrations, and not to light emitted by the sparks.

Mr. **Blakesley** enquired if lengthening the sparks produced greater effect on the copper filings.

Mr. **Lucas** asked if the resistance of a tube ever became infinite again if left for a long time.

In reply, Mr. **Croft** said the current sometimes passed before the spark actually occurred between the knobs. He had not left tubes for very long, and had not found the resistance re-appear without tapping.

## CONGRESS OF THE GERMAN SOCIETY FOR THE PROMOTION OF RATIONAL PROCESSES OF PAINTING.

According to the *Chemiker Zeitung* the Congress of this Society was held at Münich on September 28th, 29th, and 30th, and was attended by upwards of 150 chemists and artists. The Honorary President was Prof. von Pettenkofer.

Prof. Petruscheffsky, of the University of Petersburg, sent in a paper on the permanence of oil-paintings, which, in the absence of the author, was read by Prof. A. W. Keim, the founder of the Grünwald Experimental Station for Painting.

Theodor Niederländer, Chemist to the Experimental Station, read an interesting paper on the preparation and properties of cadmium yellow.

L. Lethenmayer read a paper on the ethereal oils, their applicability in painting, and their comparison with mineral oils. He recommends, as rapidly drying materials, rectified oil of turpentine, light camphor oil, and rosemary oil. Oils of lavender and spike delay drying. He insisted on the use of pure, genuine products.

The same author communicated the results of an investigation on the absorption of oxygen by certain drying oils and their acid and iodine numbers. He condemns all "dryers" which contain lead, as it forms with the oil a compound which darkens strongly in course of time. He finds that the oil of *Lallimentia iberica*, a labiate plant cultivated near Kiew, surpasses all other oils in its drying power.

Further papers were read on asphaltum, the use of which in art should be restricted as far as possible, and on strontium uranate.

There followed a discussion of a normal scale of colours, including such only as are genuine and permanent.

## NOTICES OF BOOKS.

*The Essentials of Chemical Physiology for the Use of Students.* By W. D. **Halliburton**, MD., F.R.S. London: Longmans, Green, and Co.

The author of this work, who is the Professor of Physiology in King's College, London, writes to supply students with instructions for the practical investigation of the most important subjects included under the head of Physiological Chemistry, and at the same time to furnish an elementary text-book of the subject. In both these respects he has executed his task in a most able and satisfactory manner. It has been regretfully pointed out in several quarters that, in physiology, Britain now occupies a position less creditable than she has secured in the other departments of biology, and we are by no means secure that the work before us will escape the hostile scrutiny of Victoria Street.

The author's general views, laid down in the Introduction, are judicious. He does not admit that the chemical structure of protoplasm can be studied until it has been killed. He does not deny to animals *in toto* the power of building up complex structures from simple materials. Consequently he rejects an erroneous distinction which some writers have attempted to draw between animals and plants. He does not, however, admit iodine and bromine as occasional constituents of the animal body.

In speaking of food-stuffs the author shows that the percentage of nitrogen, or even of the proteids, does not at once furnish decisive evidence as to the dietetic value. Peas and lentils doubtless contain more proteid than animal matter; but vegetable matter is less nutritious, as much of its nitrogenous matter is sparingly assimilable. Here is the refutation of one of the vegetarian dogmas.

We are glad to notice that attention is drawn to the value of the spectroscope in chemico-physiological research. In some instances where blood is required for an observation, the student is directed to obtain it by pricking his own finger—a "painful experiment upon an animal" which may be performed without any red-tape formalities.

A somewhat questionable statement is met with in the section in flour. The author writes that brown flour "is useful as a mild laxative, the insoluble cellulose mechanically irritating the intestinal canal as it passes along." We know of cases where this mechanical irritation has given rise to obstinate diarrhœa.

The crystals of oxyhæmoglobin are mentioned and figured. Here we are reminded of the perplexing fact that the form of these crystals in animals of the same order—*i. e.*, the guinea-pig, the squirrel, and the hamster—are very dissimilar. This is an argument against organic evolution which has not yet found a satisfactory explanation.

A remarkable difficulty is here mentioned referring to the poisons produced by bacteria in the animal body. They may be either alkaloidal (ptomaines) or proteids. The existence of deadly proteids is as yet a mystery, since no chemical difference has been found between them and the proteids, which are harmless and serve as foods.

The illustrations to this work are numerous, well selected, and well drawn. To students of the chemical phase of physiology this work may be safely recommended.

*A Select Bibliography of Chemistry*, 1492—1892. By HENRY CARRINGTON BOLTON. Washington: The Smithsonian Institution. 1893. 8vo., pp. 1212.

DR. H. C. BOLTON is recognised as, perhaps, the highest living authority on the bibliography of chemistry and the allied sciences, and those readers who expect to find here a very full and trustworthy book of reference will not be disappointed. The author has carefully studied the catalogues of the chief Royal and National libraries of civilised countries, and has, in the most important cases, had "access to the shelves." He has summarised the particulars of 12,031 works, not merely in the "cultursprachen," English, French, and German, but in Arabic, Finnish, Gujerathi, Hebrew, Hindi, Rumanian, and Welsh.

The work is divided into seven sections—bibliographies, dictionaries, histories, biographies, chemistry (pure and applied), alchemy, and periodicals.

The fifth section is more extensive than the remaining six taken jointly, but the author considers it the least satisfactory. It includes merely independent works, but not contributions to periodicals. The author has sought to include the applications of chemistry to the various arts, but not the arts themselves. Thus works on agricultural chemistry are admitted, but not those on agriculture. Here there is sometimes, admittedly, no small difficulty in drawing the line.

Omissions in a work of such compass must be considered unavoidable. Thus in the index we find only one work on sewage and its treatment. Two others, more widely known, but which it is not our duty to advertise, have been omitted.

The section on Alchemy may cause some amusement, though some of the works here mentioned may find earnest admirers in an age like the present, which seems inclining to the re-habilitations of views generally considered as superstitious. But we may feel surprise and regret on finding the illustrious naturalist De Lamarck combatting the Lavoisierian theory of combustion. Chenevix also condemned the "French Neologists." Towards the end of the last century, K. A. Kortum came forward in defence of alchemy. In 1889 Papus seriously undertook a proof of the existence of the philosopher's stone. In 1887 R. Mendes Teixeira attacked Wurtz and Berthelot, and attempted to show that Comte anticipitated the theoretical views of Gerhardt.

No library of a university or learned society can be considered complete if it does not possess a copy of a book at once so useful and so curious.

*Catalogue of Chemical Apparatus, Balances, Drying Ovens, Furnaces, Laboratory Stands, &c.* In Two Volumes. Also Special and General Glass Apparatus, Hydrometers, Porcelain, and Clay Ware. (At end of this list is a Complete Index for the two Lists). A. Gallenkamp and Co., 2, 4, 6, Cross Street, Finsbury, London, E.C.

THIS catalogue of chemical apparatus is exceedingly complete. Here are mentioned many of the most recently devised appliances for analysis and research. Under the various prices of apparatus we find frequently a reference to the journal or text-book in which their structure and use are described *in extenso.*

As a very useful appliance here mentioned we may notice the Gallenkamp-Heele colorimeter, which is said to give readings accurate up to 1-10th per cent.

It is to be regretted that hydrometers with the Baumé scale figure to such an extent. For this graduation no reason can be shown, especially as it exists in three different modifications, and the purchaser of an instrument cannot tell without actual experiment which type it represents. Thus in some standard works 76° B. = sp. gr. 2·000, whilst in this catalogue it appears = 2·118.

A peculiarity of this catalogue is that for a great number of articles, those especially of glass, the prices are given as in Germany and in London. The difference is surprising, if we remember that there is no import-duty.

The catalogue is stated as having been printed in Antwerp. Certainly it is rich in errors. We should beg to suggest to Messrs. Gallenkamp that, if for unknown reasons they cannot have their printing done in Britain, they would at least do well to have the MS. or the proofs very carefully read by some one acquainted with the English language.

*The Pharmacopœia of the United States of America.* Seventh Decennial Revision (1890). By Authority of the National Convention for Revising the Pharmacopœia. Philadelphia: Lippincott Co.

IN this edition we find certain principles laid down which must be considered decidedly judicious. Thus the allowable percentage of impurity is to be prescribed as closely as practicable. Chemical formulæ are to be given only in the new notation. "No substance which cannot be produced otherwise than under a patented process, or which is protected by proprietary rights, shall be introduced into the Pharmacopœia." This proviso is good, but it is not so good as the German law, which refuses patents to medicines, &c., and a still more excellent way would be to refuse protection to all processes for preparing medicines, foods, &c.

We are glad to see that the semi-barbarous notion of "proof" is abandoned as regards alcohol and its mixtures. In its stead, the specific gravity is laid down. There are comparative tables of measures according to the metric system, the American customary system, and the British system. This is the more necessary, as the pints, gallons, &c., of the two latter are by no means equal. The American grain is, however, identical with the British grain.

We find no comparative tables of hydrometric scales, and hence we cannot say whether Baumé's scale has been abandoned or not.

*Practical Work in Heat.* For Use in Schools and Colleges. By W. G. WOLLCOMBE, M.A., B.Sc., Senior Science Master in King Edward's High School, Birmingham. Oxford: Clarendon Press, 1893. 8vo., pp. 61.

THE author very justly remarks in his Preface that "the chief value of a scientific education consists not so much in storing the mind with a large number of facts as in the training of the powers of accurate observation and reasoning." He might have usefully said "inductive reasoning." He considers that a course of experimentation in heat is one of the best means to this end.

The experiments to be performed are very judiciously selected for the purpose in view, and are remarkable for the simplicity of the apparatus required. Hence no objection can be raised by the heads of schools on the score of expense.

The operations are arranged under the heads of thermometry, expansions, calorimetry, evaporation, and radiation.

This excellent little book is a proof that in the High Schools the ice of mediæval pedantry is beginning to melt.

*Electric Light Installations.* Vol. I., *The Management of Accumulators.* A Practical Handbook. By Sir David Salomons, Bart., M.A., V.-P. Inst. Elect. Engineers, Assoc. Inst. C.E., Memb. Amer. Inst. Elect. Engineers, Memb. de la Soc. Int. des Elect., Memb. Phys. Soc., &c. Seventh Edition, Revised and Enlarged. An Edition, mostly Re-written, of Electric Light Installation and the Management of Accumulators. London: Whittaker and Co., G. Bell and Son. 1893.

When a technical work has reached its seventh edition we may feel confident that it must meet a widely-felt public want. The treatise before us has thus fairly "won its spurs." We find here a description of accumulator-cells and their mode of employment, instructions for setting up the cells and the accumulator-house for charging and discharging. A very important chapter is that on failures, with their causes and remedies. There are instructions for testing a section, but with the remark that there is no method at present known for testing a cell satisfactorily in a short time. In the final chapter, or summary, we are told that no rules "unmixed with brains" are of the least service.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 16, October 16, 1893.

**Certain Properties of Lead Oxides.**—A. Bonnet.—If we mordant cotton in an alkaline plumbate and wash it in much water, there takes place dissociation in favour of the fibre, which becomes loaded with the puce lead oxide. The oxidising power of this substance occasions the destruction—more or less complete—of the fibre. The same phenomenon of dissociation occurs with the plumbites, without the inconvenience of oxidation. The white oxide thus deposited, in addition to the known properties of the lead compound, effects a series of other reactions. Cotton mordanted and steeped in baths of logwood, sumac, fustic, &c., forms immediately, especially in heat, a coloured lake, black with logwood, yellowish green with sumac, and bright yellow with fustic. The tannins and the catechus are strongly attracted. By means of this mordant we may also deposit upon cloth the majority of metallic oxides on using suitable baths. Gold, silver, mercury, vanadium, manganese, chrome, iron, cobalt, nickel, and zinc give very distinct reactions using neutral salts in hot solutions. These reactions are so sensitive that with a bath of potassium permanganate at 0·25 grm. per litre we can obtain at 80°—90° a good bronze deposit of manganese peroxide. Traces of vanadium in an ammonium chloride are rendered manifest, and give a yellowish deposit with the salts of aromatic amines. This displacement of the oxides of different salts is explained by the formation of lead salts soluble in heat. It is thus that the iron, cobalt, nickel, and chrome salts are decomposed in heat and give on the fibre a deposit of the corresponding oxide, whilst there is formed in the bath a lead chloride soluble in heat, but precipitable on cooling.

**Internal Temperature of Bread when Drawn from the Oven.**—M. Ballard.—We are led to infer from these experiments, made in different ovens, on loaves and cakes of different size and shape, with paste risen and not risen, that the temperature of the crumb reaches from 100°—102°. That of the crust is distinctly higher.

*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., Nos. 17 and 18.

**Sulphones of Benzylic Alcohol and of Benzoic Acid.**—P. Genvresse.—The author has obtained and examined the dibromhydrine of the sulphone of benzylic acid, the sulphone of benzylic alcohol, that of benzoic acid, and that of silver benzoate.

**Constitution of the Colouring-matters of the Rosaniline Group.**—M. Prudhomme and C. Rabaut.—Rosenstiehl has established that the colouring-matters of the rosaniline group may form acid salts (hydrochlorates or hydrobromates) containing an atom of Cl or of Br more than the molecule contains atoms of nitrogen. This result is possible only if one of the atoms of chlorine or of bromine is directly linked to the methanic carbon. The facts which the authors expound seem to support this view.

**On Benzoylcinchonine.**—E. Léger.—The author has obtained this compound in crystals, and has examined its basic hydrochlorate, neutral hydrochlorate, basic hydrobromate, chloroplatinate, monoiodomethylate, diiodomethylate, iodoethylate, and bromomethylate. In all these compounds it is easy to recognise the presence of the benzoyl radicle by means of the reaction of Ferreira da Sylva.

**Combination of Albumenoid Matters and of Hematines Extracted from the Blood of Various Animals.**—H. Bertin-Sans and J. Moitessier.—The authors have succeeded in obtaining solutions presenting the spectral reactions of hæmoglobine by combining the hæmatine of the ox with the albumenoid matter extracted from the blood of sheep.

**Method for Rapidly Demonstrating the Displacement of Carbon Monoxide of Carboxyhæmoglobine by means of Oxygen.**—H. Bertin-Sans and J. Moitessier.—Into 50 c.c. of distilled water the authors pour 10 to 12 drops of blood saturated with carbon monoxide. Into 10 c.c. of the solution of carboxyhæmoglobine thus obtained they pass a rapid current of air for four minutes. On taking 50 c.c. of the solution thus obtained and adding an equal volume of a solution of 20 per cent NaOH and 4 to 5 drops of ammonium sulphide, the liquid, if examined in a thickness of 2 c.m., quickly presents the spectrum of hæmochromogen, which detaches itself very distinctly from the very attenuated spectrum of the carboxyhæmoglobine not yet decomposed.

**Composition of the Honey-dew of the Lime Tree.**—L. Maquenne.—The product seems to be melezitose, an isomer of raffinose.

**Citric Fermentation.**—Charles Wehner.—Not suitable for insertion.

No. 19.

**A New Reaction of Eserine, and on a Green Colouring-matter Derived from that Alkaloid.**—A. J. Ferreira da Silva.—A small fragment of eserine, or of one of its salts, of the size of a small grain of sand, is placed in a small porcelain capsule, and dissolved in one or two drops of fuming nitric acid. The light yellow solution thus obtained, on evaporation on the water-bath, turns successively to deep yellow and then to orange; but if it is evaporated to dryness whilst being constantly stirred with a glass rod, the colour of the residue passes to a pure green. The green matter thus obtained is soluble in water, and more readily in strong alcohol. The solutions are perfectly green, non-fluorescent, and on evaporation leave the colouring-matter unchanged. The solution of the matter in hot dilute nitric acid is very distinctly fluorescent; it is blood-red by reflected and greenish yellow by transmitted light. The watery solution of the green matter, if examined with the spectroscope, is characterised by two absorption-bands; the more distinct is placed in the red, between $\lambda$ 670 and $\lambda$ 688. The other, which is broader, but less distinctly defined, occupies a part of the indigo and the violet, especially by $\lambda$ 400 and $\lambda$ 418. There is also a very faint band in the orange. The author proposes the name chloreserine for this substance, and purposes continuing its study.

## MISCELLANEOUS.

**Book Catalogue.**—The firm of J. B. Baillière and Son, 19, Rue Hautefeuille, Paris, has just published a Bibliography of the Chemical Sciences, which contains a detailed description of more than than three thousand works on modern and ancient chemistry, in French and other languages. This pamphlet of 80 pages 8vo., double columned, will be sent gratis and post-paid to all chemists who write to Baillière and Son for a copy.

**An Improvement in Gas Burners for the Laboratory.**—All chemists in active laboratory work must have been struck by the rapid deterioration undergone by the gas burners used for boiling and igniting. Oxidation, under the influence of the heat and acid vapours, proceeds at an enhanced rate, and, in spite of frequent scraping and painting with Brunswick black, the burner soon becomes shabby and dilapidated. Messrs. Fletcher, Russell, and Co., the well-known gas engineers of Warrington, have submitted for our inspection one of their laboratory burners in which it is anticipated this great defect has been overcome. We have had it in use for some time, and it shows no signs of rust or deterioration at present. The cast-iron burner is coated on the surface by what is called Chimatto enamel, which is unchanged by a red heat continued for any length of time, and does not chip off. All colours, either dead or bright, and both gold and silver, either dead or polished, are obtainable on the same casting, and all alike are unchangeable, either with exposure to air or to any heat up to a bright red.

**The Franklin Institute.**—We have received the programme of lectures of this Institution for the Sessions 1893—1894. Among the lectures announced there are two by Horace Pettit on the law of inventions, and one on a plea for the study of forestry in the lower schools—a very important subject. Prof. S. P. Sadtler will give a review of recent progress in chemical technology; Prof. S. P. Sharples, on the fat and soap industries; Rudolph Hering, on the purification of water; Dr. C. S. Dolley, on economic botany in relation to modern civilisation; and Prof. E. Hart, on the number of the forms of carbon. O. Chanute, C.E., will lecture on aërial navigation—a subject of intense interest to the criminal classes and to conspirators. The library of the Institute comprises above 38,000 volumes, 24,000 pamphlets, the same number of charts and maps, and over 1100 photographs, all classified and catalogued.

**Thermic Study of the Acid Functions of Camphoric Acid.**—G. Massol.—The second function of camphoric acid is thermically weaker than the acid function of the organic acids.—*Bull. de la Soc. Chim. de Paris.*

**Photography in the Service of Chemistry and of the Practical Chemist.**—E. Valenta.—Under this title the *Chemiker Zeitung* publishes an important paper, from which we make the following extracts:—The acquirement of photography will always be of eminent service to the chemist. If engaged in metallurgy he can, by means of photography, prepare exact representations of the fracture of different metals, which will much facilitate the study of the different steels and irons in connection with their proportions of manganese, silicon, carbon, &c. The chemist concerned with the investigation of foods will often have occasion to make use of photography. A correct photograph of a microscopic preparation recognised as decisive evidence of sophistication may serve in support of the opinion which can be submitted to a court. In bacteriology photographs are more decisive than the best drawings or descriptions. The chemist requires for his purposes chiefly an accurate knowledge of the negative process with silver-bromide gelatin dry plates, and the simplest positive process. He must especially beware of portrait photography. For purely technical purposes he may acquire all that is necessary in one or two months.

## MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Chemical Industry, 8. "Spirit Assaying by Weight," by J. Scarisbrick. "Estimation of Alizarin and Allied Colouring Matters," by P. W. Dreaper.

Friday, 10th.—Physical, 5. "On the Separation of Three Liquids by Fractianal Distillation," by Prof. S. Young, F.R.S., Prof. Barrett, and Mr. Thomas. "On the Critical Constants of Various Ethers," by Prof. S. Young, F.R.S. "An Instrument for Drawing Conic Sections," by J. Gillett, B.A.

THE CHEMICAL NEWS.

Vol. LXVII., No. 1772.

## SALTS OF A NEW PLATINUM-SULPHUREA BASE.*

By W. J. SELL and T. H. EASTERFIELD.

Various platinum thiocarbamide compounds have been prepared by Professor Emerson Reynolds and by Rathke, but no derivatives of the base $Pt(CSN_2H_4)_4(OH)_2$ have been hitherto described. The chloride of this base is readily prepared by adding platinic chloride solution to a boiling solution of sulphurea in dilute hydrochloric acid. The filtered solution deposits crystalline needles of the chloride when mixed with strong hydrochloric acid, in which the chloride is very sparingly soluble. Analysis agrees with the formula $Pt(CSN_2H_4)_4Cl_2$.

The sulphate, $Pt(CSN_2H_4)_4SO_4$, is precipitated in regular octahedra when dilute sulphuric acid is added to an aqueous solution of the chloride.

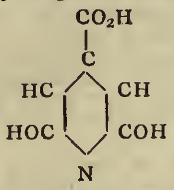
The picrate, $Pt(CSN_2H_4)_4Pk_2$, is very sparingly soluble in cold water; it crystallises from hot water in beautiful golden-yellow iridescent needles.

The free base, $Pt(CSN_2H_4)(OH)_2$, has not been isolated in the pure state.

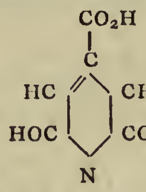
## ON CITRAZINIC ACID.*

By W. J. SELL, M.A., and T. H. EASTERFIELD, M.A.

Citrazinic acid was first prepared by Behrmann and Hoffmann, who obtained it by the action of sulphuric acid upon citramide; they assigned to it the formula—



A study of the reactions of the acid causes the authors of this paper to regard the formula—



tantomeric with that of Behrmann and Hoffmann, as more generally satisfactory. The following facts appear to support this formula.

1. Citrazinic acid is readily prepared from all anhydro-aconitic derivatives, and is therefore most simply regarded as a condensation product of aconitamide.

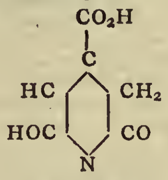
2. Guthzeit and Dressel have shown that citrazinic acid is readily re-converted into aconitic acid.

3. Only two classes of salts, $C_6H_4M'NO_4$ and $C_6H_3M'_2NO_4$, can be prepared.

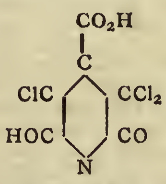
4. Chlorine produces trichlor-substitution derivatives, from which two of the chlorine atoms are much more readily removed than the third chlorine atom. Similarly, bromine gives rise to tribrom-citrazinic acid.

5. Diazobenzene chloride reacts with citrazinic acid to produce phenyl-hydrazo (?) citrazinic acid.

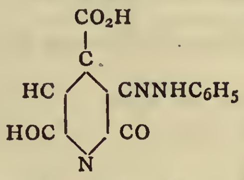
6. Nitrous acid converts citrazinic acid into an iso-nitroso compound, which when warmed with dilute sulphuric acid looses carbon dioxide and yields a quinhydro compound dissolving in alkalis with the production of an intense blue colour. Oxidation converts the quinhydrone into a quinone, resembling ordinary quinone in its appearance and behaviour. The following formulæ illustrate these relationships:—



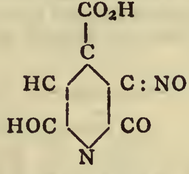
Citrazinic acid.



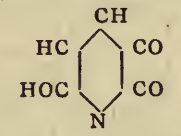
Trichlor-citrazinic acid.



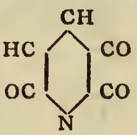
Phenyl-hydrazo-citrazinic acid.



Iso-nitroso-citrazinic acid.



Quinhydro-keto-pyridin.



Quino-keto-pyridin.

### ON THE
## TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

One of the greatest difficulties connected with the teaching of Inorganic Chemistry in any systematic lecture-course arises from the great amount and diverse nature of the material which has to be dealt with, and this difficulty, so far from diminishing, will certainly increase as the science developes. Even now it is practically impossible in any lecture-course of the usual length to treat of matters such as the student of to-day may legitimately expect to have brought under his notice. The broad, general principles of the science are, on the whole, adequately considered in so far as they can be illustrated by the study of the non-metallic elements and the compounds which they form by their mutual union. So large a proportion of the course is, as a rule, occupied with these matters that but scant attention can be paid to the metals. Generally only the more technically important of these are considered, with special mention of their modes of extraction, their uses, and the commercially valuable salts which they yield, while whole groups of metals, and particularly the so-called rare metals, are seldom even mentioned, in spite of the fact that their chemistry is of considerable theoretical importance. These facts will be patent to every teacher. The problem is to find a remedy. There is no doubt that the teaching of modern Organic Chemistry, in any course at all commensurate with the importance of the subject, is more systematised and better arranged than the courses in Inorganic Chemistry, which are too frequently trammelled by traditions and text-books.

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* Read before the British Association (Section B), Nottingham Meeting, 1893.

In a recent lecture to the Fellows of the Berlin Chemical Society* Professor Lothar Meyer, one of the most eminent and experienced of German teachers, has sought to indicate a remedy for the present condition of things, which it is the object of this paper to explain. As the result of much thought and of personal practice he has elaborated a system which, in a course of about eighty lectures, enables him to take a fairly comprehensive survey of the present aspect of Inorganic Chemistry without prejudicing or in any way sacrificing the consideration of the fundamental principles of the science. The basis of his method rests upon the application of the Periodic or Natural System of classification of the elements, which he has done so much to elaborate and popularise. Similar attempts have, it is true, been made by other teachers, but their method has consisted only in the partial adoption of this principle. It must be confessed that the greater number of teachers at the present time content themselves with merely mentioning the existence of what is called the Periodic Law, and make little or no practical application of it in the arrangement of their lecture-courses. Professor Lothar Meyer seeks to show how this generalisation may be made use of from the beginning of a course of lectures adapted to beginners.

Taking the Natural System of the Elements in its usual form, there is in the outset some difficulty in determining where to begin. At first sight one of the groups of Family I. seems most naturally to constitute a starting-point, and, although it is contrary to the general custom of commencing with the non-metals, Prof. Lothar Meyer has tried this method and found it impracticable. To begin with the seventh Family and work backwards through the different families, whereby hydrogen, chlorine, oxygen, sulphur, nitrogen, and carbon are first treated, more nearly resembles the usual method; but it has disadvantages, for chloric and perchloric, sulphuric, nitric, and phosphoric acids, and generally the oxides of these families, do not belong to the simpler compounds, and therefore the systematic progression from simple to complex relations is reversed. We cannot lose sight of the fact that, among the non-metals which form compounds with oxygen, the hydrogen compounds are the simplest of all. In order to arrive at a feasible and just division of the material, Prof. Lothar Meyer found it necessary to adopt certain re-arrangements, whereby it was possible to follow the order in the Natural System, to take the student from the simple to the more complex compounds as in organic chemistry, to make clear to him analogies and differences, and to give him uuch a comprehensive survey of the great variety of substances that he can himself easily deduce the composition and also the behaviour of any compound so soon as the position of the element in question is noted in the system.

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | | |
|---|---|---|---|---|---|---|---|---|---|
| Li | Be | B | C | N | O | F | | | |
| Na | Mg | Al | Si | P | S | Cl | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni |
| Cu | Zn | Ga | Ge | As | Se | Br | | | |
| Rb | Sr | Y | Zr | Nb | Mo | — | Ru | Rh | Pd |
| Ag | Cd | In | Sn | Sb | Te | I | | | |
| Cs | Ba | La | Ce | — | — | — | | | |
| — | — | Yb | — | Ta | W | — | Os | Ir | Pt |
| Au | Hg | Tl | Pb | Bi | — | — | | | |
| — | — | — | Th | — | U | — | | | |

Dr. Lothar Meyer begins his course by defining the position of chemistry among, and its relations to, the other natural sciences. The relation of chemistry to physics is explained by a series of contrasted experiments, some showing purely physical, others chemical phenomena: for example, platinum wire glows while magnesium wire burns in a flame; iron is magnetised and rusts; sulphur is electrified by rubbing, while phosphorus is inflamed; nitre dissolves in water and re-crystallises out unchanged, and zinc dissolves in sulphuric acid and re-crystallises as zinc sulphate; &c., &c.

After the various subdivisions of chemistry and its relations to other branches of knowledge have been spoken of, and the literature surveyed in some detail, Dr. Meyer then proceeds to give a brief account of the science. The chemistry of the Egyptians and Arabians, of the Alchymists and Iatrochemists, is rapidly dealt with; some little time is spent on Van Helmont's teaching; and the theory of phlogiston is gone into pretty fully, all that can be said in its favour being first stated, when its weaknesses are exposed, all of which naturally leads to the consideration of Lavoisier's doctrine.

We are thus brought to the question of the constitution of the air, and to the nature of oxygen, which, because it is the most widely distributed of all substances and occurs in largest quantities, is now fully treated of and in the usual way. Incidentally the student learns something of nitrogen, and to now distinguish it from some of the gaseons products of combustion, especially from those of carbon and sulphur. By the discussion of Lavoisier's doctrine, his imperfect explanation of the cause of the heat of combustion is mentioned, together with Rumford's experimental proofs that heat is a form of motion. For the complete exhaustion of the subject of the phlogiston theory, the nature of the substances which were looked on, more or less, as pure phlogiston, must be examined, and, above all, the nature of hydrogen. With the discussion of it the usual experiments are given. Eudiometry affords an opportunity of speaking of the volume relations according to which gases combine, and also of the methods for the determination of density by which volume and weight are calculated, and electrolysis is demonstrated as a means of separating the constituent parts of a compound.

Water is now dealt with in detail, and special stress is laid on the constancy of the combination of hydrogen and oxygen, and a short account of stoichiometry and of the atomic theory is given incidentally. After, with water and air as examples, Lavoisier's thorough method of distinguishing elements and their compounds has been explained, the student can easily see that besides the three elements already spoken of — oxygen, hydrogen, and nitrogen,—there must be many more. Dr. Meyer then, following the example of his own teacher, Bunsen, gives a general, but rapid, survey of all the known elements, which has the advantage of not disturbing the order; and if at any time in the course of the lectures a compound is mentioned whose elements have not yet been minutely described or experimented with, the student has only to recall this survey.

This survey is given in approximately three lectures in the following order. Next to the gases already described come first of all the gaseous, then the volatile and easily fusible non-metals:—Fluorine, Chlorine, Bromine, Iodine, Sulphur, Selenium, and Phosphorus. Of these only the

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* *Ber. d. Deut. Chem. Gesell.*, xxvi., 1230, 1893.

most important properties are explained, especially the capabilities of the salt-formers, of sulphur, and of oxygen to support combustion, and, on the other hand, the inflammability of sulphur and of phosphorus is demonstrated.

The difficultly or non-fusible non-metals follow:—Carbon, Silicon, and Boron.

Then come the semi-metals and easily fusible:—Tellurium, Germanium, Arsenic, Antimony, and Bismuth; and the difficultly fusible:—Chromium, Molybdenum, Tungsten, Uranium, Ruthenium, and Osmium.

With these Rhodium and Iridium together form, on the one side, and Manganese on the other, the connecting links with the true ductile metals of the platinum and iron groups:—Platinum, Palladium, Iron, Cobalt, and Nickel.

The less difficultly fusible—Copper, Silver, and Gold—follow, the best conductors of heat and electricity, then the eighth easily fused heavy metals—Zinc, Cadmium, Mercury, Gallium, Iridium, Thallium, Tin, and Lead.

The light metals conclude the survey,—first of all Aluminium, with its rare allies, then Magnesium and Beryllium, and finally the metals of the alkaline earths—Calcium, Strontium, and Barium—and of the alkalies—Lithium, Sodium, Potassium, Rubidium, and Cæsium.

Of each of these elements only so much is said as is requisite and sufficient to characterise them, and at the same time to bring out their association with the common things of daily life, and, as far as possible, matter of historical interest is introduced.

(To be continued).

## THE CHEMISTRY OF PLANT FIBRES: CELLULOSES, OXYCELLULOSES, AND LIGNOCELLULOSES.[*]

By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

In a series of papers, 1880—93, we have dealt with special points in the chemistry of the constituents of the plant fibres. Our recent investigations have furnished data which enable us to consolidate this previous work into a more complete account of the lignocelluloses, and at the same time to exhibit a probable connection of the process of lignification with the general chemistry of the celluloses proper, through their oxidised derivatives, or oxycelluloses.

Without drawing any final conclusion as to the genetic relationships of the members of these several groups, we shall be able to show that in the jute fibre—the simplest type of lignification—the characteristic keto-R-hexene group is linked to the normal cellulose of the fibre through a series of oxidised and condensed derivatives, which are in constitutional features so related to the cellulose on the one hand and the R-hexene constituent on the other as to suggest a series of transitions from the one extreme member to the other.

As is well known, the non-cellulose constituents of jute are converted into soluble derivatives by a variety of treatments under which the cellulose remains more or less unaffected. Thus, by chlorine gas the keto-R-hexene groups are converted into quinone chlorides, soluble in sodium sulphite solution. The residue from this treatment is a lustrous white cellulose preserving the structural characteristics of the original fibre and amounting to 75—80 per cent of its weight.[†] Bromine (as bromine water) acts much less completely. After exposure to this reagent for some hours, and boiling the brominated fibre with dilute alkaline solution, much of the non-cellulose remains, and the treatment requires to be once or twice repeated before arriving at a pure cellulose. When obtained, it is usually much more disintegrated than that from the single treatment with chlorine, and amounts to 72—75 per cent. The diminished yield is due to attendant oxidation and hydrolysis of a constituent which we shall subsequently describe as cellulose $\beta$. In addition to these actions of the halogens, there are processes by which the non-cellulose is attacked and dissolved in a single treatment. We cite two as typical, and of very opposite character:—(*a*) Digestion with dilute nitric acid at 70—80° (*Ber. Deut. Chem. Ges.*, xxiv., 1186, 1772), and by digestion with solutions of bisulphites at 130—150° C. The residue from these experiments is a cellulose, obtained as a disintegrated mass or pulp and amounting to 60—63 per cent of the weight of the fibre. This more resistant cellulose we may describe as cellulose $\alpha$. An important feature of distinction of these celluloses from one another is the presence in the cellulose $\beta$ of the $O.CH_3$ group (*infra*). But for the present we are rather concerned with their common differentiation from the typical cotton cellulose. The jute cellulose, however obtained, has, in fact, the composition of an oxycellulose; that is, the carbon percentage is 43 or less, and the reactions are such as to indicate the presence of ketonic or aldehydic oxygen.

We are now able to give a more conclusive proof of its constitutional relationship to the oxycelluloses in the results of a new hydrolysis of their group of compounds; which consists in treating with a reagent prepared by saturating aqueous sulphuric acid of 1·5 sp. gr. with hydrochloric acid gas.[*] In this acid the oxycelluloses dissolve completely, and on diluting and distilling furfural is obtained in quantity. We determined the yield of this aldehyd from such celluloses as we have previously noted to be differentiated from the normal type, viz.,—

| | | Furfural. |
|---|---|---|
| Straw cellulose yielded | .. .. .. .. .. | 14·5 per cent |
| Wood ,, ,, | .. .. .. .. .. | 6·5 ,, |
| Jute ,, | (Cl method) yielded .. .. | 6·0 ,, |
| Jute ,, | ($HNO_3$ method) yielded .. | 6·0 ,, |

These quantities are considerable, and sufficient to indicate differences of constitution.

We then examined typical celluloses of the normal and more resistant type—resistant, that is, to oxidation and hydrolysis. The following yields were determined:—

| | Cellulose. | Per cent. |
|---|---|---|
| Fibres bleached by alkaline hydrolysis and hypochlorite oxidation. | Cotton yielded .. .. | 0·2 |
| | Flax ,, .. .. | 0·7 |
| | Rhea ,, .. .. | 0·5 |

The fibres in the above cases were disintegrated by the reagent, but not dissolved. It appeared that the yield of furfural might be proportional to the degree of oxidation of the celluloses attending the process of bleaching or purification. In verification of this, we oxidised cotton in successive stages by a method admitting of more exact control than those which have been previously used, viz., by chromic acid in dilute solution and in presence of sulphuric acid, in quantity equivalent to the resulting $Cr_2O_3$. The products were treated with the reagent, and the solutions, after dilution, were distilled for furfural. The numbers obtained are appended:—

| | Weight of cotton. | Weight of $CrO_3$. Grms. | Volume of solution. C.c. | Oxy-cellulose. Per cent. | Yield of furfural. |
|---|---|---|---|---|---|
| (*a*) | 4·7 | 1·5 | 70 | 93·0 | 4·1 |
| (*b*) | 4·7 | 3·0 | 90 | 87·0 | 6·3 |
| (*c*) | 4·7 | 4·5 | 110 | 82·3 | 8·2 |

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[*] From the *Ber. Deutsch. Chem. Gesell.*, November, 1893.

[†] We have analysed this cellulose on several occasions, and find it gives uniform numbers, viz., C, 42—43; H, 6·0. (*Chem. Soc. Journ.*, xli., 104).

[*] The reagent is most conveniently made by mixing concentrated sulphuric and aqueous hydrochloric acids; at 1·56 sp. gr. the acid contains 57·3 per cent $H_2SO_4$ and 5·5 per cent HCl.

The oxycellulose (*c*) was entirely dissolved by the reagent; (*b*) and (*a*) incompletely. The specimen (*c*) on ultimate analysis was found to contain 41·9 per cent carbon.

In further elucidation of these relationships, we have studied the oxidation of other typical carbohydrates, but of lower molecular weight. Starch, cane-sugar, and milk-sugar were treated with chromic acid in dilute solutions in the cold, and in presence of HCl in equivalent quantity. The quantities of chromic acid (weighed as $K_2Cr_2O_7$) used represent approximately 1, 2, and 3 atoms O upon a formula weight $C_6H_{12}O_6$ (=180). The oxidation completed, the products were distilled from hydrochloric acid and the furfural estimated in the distillate.

| Carbohydrate. | Weight. | $K_2Cr_2O_7$ used to oxidise. | Yield of furfural per cent of original carbodrate. | |
|---|---|---|---|---|
| | Grms. | Grms. | (1) | (2) |
| Milk-sugar .. .. | 5·5 | 3·0 | 6·2 | 6·6 |
| ,, .. .. | 5·5 | 6·0 | 10·5 | |
| ,, .. .. | 5·5 | 9·0 | 10·0 | |
| Cane-sugar .. .. | 5·5 | 3·0 | 4·0 | |
| ,, .. .. | 5·5 | 6·0 | 7·0 | |
| Starch .. .. .. | 5·5 | 9·0 | 11·0 | |
| Starch (previously swollen with water | 5·5 | 9·0 | 10·3 | |

It appears, therefore, to hold generally that the hexoses, or carbohydrates immediately derived from them, are converted by regulated oxidation into products which yield furfural on hydrolysis. It is, of course, possible that the formation of a pentose may precede that of furfural; and, if so, that in that sense the pentoses are produced from the hexoses by oxidation. This question is being further investigated. In the meantime, it is important to remember that the formation of furfural from a carbohydrate by hydrolysis affords no conclusive evidence as between a hexose or pentose configuration of the parent substance.

By these results, therefore, the oxidation of the hexoses and their derivatives generally, and of normal cellulose in particular, is directly connected with the production of furfural-yielding carbohydrates, and the probability at once arises that these two groups of "natural" products may be similarly related in the plant. There is a good deal of collateral evidence of the existence of such a relationship, but as the purpose of this communication is limited, we shall not attempt to deal with physiological points.

We have already stated that jute cellulose isolated by the process of chlorination is a mixed product, and the evidence of the variation in yield, according to the methods generally employed, warrants the division, already indicated, into—

Cellulose *α*, constituting from 60—63 p.c. of the fibre; and—

Cellulose *β*, ,, ,, 15—20 ,, ,,

Having observed the formation of derivatives containing the methyl group in various decompositions of the lignified fibres and of purified celluloses, we were led to examine certain of these for the presence of methoxyl. We have made quantitative estimations of $O.CH_3$ in jute celluloses by the well-known method, and find in the celluloses isolated by the chlorination process, *i.e.*, the mixture of the *α* and *β* celluloses,—

1·2 per cent $O·CH_3$;

whereas, in the celluloses from the treatments with dilute nitric acid and with bisulphites, *i.e*, the *α* cellulose, there is none present. Since, therefore, the cellulose *β* constitutes about one-fifth of the aggregate of cellulose in the former case, it may be calculated to contain—

$$5 \times 1·2 = 6·0 \text{ per cent } O.CH_3.$$

Representing this cellulose *β* by the formula $C_{18}H_{32}O_{16}$ (C=42·8 per cent), corresponding with the composition of the aggregate, we may express the result as follows:—

| $O.CH_3$ found. | Calculated for $C_{17}H_{29}O_{15}.OCH_3$. |
|---|---|
| 6 0 per cent | 6·0 |

We have here, therefore, a fibrous cellulose which may be described as fairly resistant to oxidation and hydrolysis—having survived the treatments of this nature—containing an ethereal alkyl group, and our views of the constitution of the celluloses as a group must receive a corresponding extension.

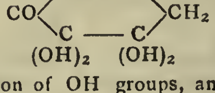
With regard to the composition and constitution of the jute fibre, it remains now to deal with the non-cellulose groups, and to apply the foregoing results to showing the connection of these groups with the cellulose.

It will be convenient if we give a brief statement of the numerical data which have from time to time been determined, and from which we shall deduce the more simple and complete view of the constitution of this group of natural products.

(*a*) *Empirical Analysis* in normal specimens of the fibre is 46—47 per cent, and the empirical formula $n(C_{12}H_{18}O_9)$ fairly expresses the mean composition of the organic constituents of the fibre.

(*b*) *Hydrolysis.*—The alkalis and more stable acids in dilute solution attack the fibre as a whole; the portions rendered soluble have the same empirical composition and reactions as the original fibre, and the fibrous residue, though it may have undergone structural changes, is similarly characterised. We have prepared a series of osazones from the soluble products, which are well defined compounds crystallising from toluene. We shall deal with these in a subsequent communication. For our present purpose it is sufficient to note that by simple hydrolysis all the constituent groups of the fibre are simultaneously attacked, and it is only when other conditions are added that these groups are more or less resolved. Such *complex hydrolyses* as are determined by nitric acid, sulphurous acid, and the bisulphites need only be mentioned in regard to their main action, which is to react synthetically with the non-cellulose constituents, forming soluble compounds, and at the same time to hydrolyse a constituent which by other treatment may be isolated as a cellulose (*β*). The residue resisting their action we have termed cellulose *α*.

(*c*) *Chlorination and Formation of Quinone Chlorides.*—The fibre substance takes up 7—8 per cent of its weight of Cl, and the reaction appears to be simple, *i.e.*, unattended by oxidation. The chlorinated derivative isolated by solvents has the formula $C_{19}H_{18}Cl_4O_9$. It contains mairogallol or leucogallol in union with a group yielding furfural and acetic acid on hydrolysis (HCl). Expressing the derivative as $3C_{19}H_{18}Cl_4O_9$, and subtracting a molecule of a quinone chloride of corresponding formula, *i.e.*, $C_{57}H_{54}Cl_{12}O_{27} - C_{18}H_6Cl_{12}O_9$, we are left with the Cl-free complex $C_{39}H_{48}O_{18} = 3C_{13}H_{16}O_6$. The two remaining constituents of the fibre substance are therefore the keto-R-hexene derivative, which we assume to contain groups of the general form*—



condensed by union of OH groups, and the empirical aggregate $C_{13}H_{16}O_6$, which remains to be further characterised.

(*d*) *Furfural Estimations.*—We have re determined the yields of furfural from the fibre substance and its derivatives, using the improved method of Tollens. The celluloses isolated by the usual methods give only fractional yields when boiled with hydrochloric acid. The fibre

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* We make no attempt to assign definite relative positions to what may be regarded as the component groups of this molecule, *i.e.*, $CO, CH_2 = C$, &c.

itself (lignocellulose), on the other hand gives considerable yields.

The following numbers have been obtained* :—

| | |
|---|---|
| Raw fibre (pure specimens) .. .. | 9·2 per cent |
| Fibre (*previously chlorinated*) .. | 9·6 „ |

and they establish the following points :—The cellulose of the fibre under hydrolysis by HCl yields traces only of furfural, which is therefore produced mainly from the non-cellulose constituents. The hexene groups obviously contribute none, and the complex $C_{13}H_{16}O_6$ is therefore the main source of this aldehyd, though it is possible that some quantity may be derived from the group which furnishes the cellulose $\beta$.

We note here that it has become customary to assume that the formation of furfural from vegetable products is evidence of the presence of a pentaglucose. But quite apart from the results communicated in the earlier part of this paper, the empirical formula we have deduced for the furfural yielding groups is altogether at variance with any such view in this case; and by the further evidence we have to adduce, is practically excluded.

We have frequently shown that acetic acid is produced in the simpler hydrolytic decomposition of lignified fibres, and we have been able to trace this to the presence of $CO.CH_2$ residues in the non-cellulose groups. Another source of products of decomposition containing the $CH_3$ group we now find in the presence of methoxyl groups.

(*e*) *Methoxyl Determinations.*—We made two estimations of $O.CH_3$ in pure specimens of the fibre. The numbers obtained were—

| | (1). | (2). |
|---|---|---|
| $O.CH_3$ per cent of fibre substance.. .. | 4·5 | 4·6 |

Of this, a portion is derived from the cellulose, as already stated. We found that the cellulose isolated by the Cl method, which gives the simplest resolution into cellulose and non-cellulose, yields 1·2 per cent $O.CH_3$. Calculating that the 80 per cent of cellulose in the fibre will yield 0·96 $O.CH_3$, and deducting this quantity, the *non-cellulose* will contain the balance, *i.e.*, 3·6 per 100 parts of fibre substance.

Further, as the non-cellulose amounts to 20—25 per cent of the weight of the fibre, the proportion of $O.CH_3$ in the non-cellulose cannot be less than four times this, *i.e.*, 14·4 *per cent.* Expressing this in molecules, the minimum is $2.O.CH_3$ in the formula weight $C_{19}H_{22}O_{10}$ (calc. 15·1 per cent $O.CH_3$).

(*f*) *Oxidation by Chromic Acid.*—The fibre substance is only very slowly acted upon by chromic acid in presence of sulphuric acid at ordinary temperatures. The mean result of an extensive series of experiments under these conditions may be stated as follows:—

Oxidised with 50 per cent of the weight of $CrO_3$, the fibre loses 10 per cent of its weight.† The colour of the product is white, with a tinge of green due to residual $Cr_2O_3$. The carbon percentage in this fibrous product is 43—44 (extreme results of several analyses). The keto-R-hexene constituent is the first to undergo oxidation, the $C=C$ union being resolved, and the product behaving as a saturated compound.

Distilled with HCl for furfural, the yield is 8—9 per cent. The configuration of the furfural-yielding groups appears, therefore, to be unaffected by the oxidation. They appear to be converted, together with cellulose $\beta$, into an oxycellulose, the product losing 30 per cent of its weight on treatment with dilute alkalis; the ultimate yield of the more resistant cellulose being, as in other oxidising treatment, 60 per cent of the weight of the fibre.

(To be continued.)

ON THE

# ACTION OF IODINE ON SOME PHENOLS AND ALLIED COMPOUNDS IN PRESENCE OF FREE ALKALI, AND A NEW CLASS OF DERIVATIVES RESULTING THEREFROM.

By THOS. R. CARSWELL.

(Concluded from p. 216).

### *On the General Structure and Positions of the Iodine Atoms.*

In the constitutional formulæ used to express the supposed structure of the various molecules and individual positions of atoms several well-marked similarities have been assumed throughout. For instance, in all cases molecular condensation is represented as having taken place, and this even in cases where two contiguous carbon atoms of two benzene nuclei have become common. One consequence of this is the assumed existence of somewhat redundant-looking molecules.

Nevertheless, the great similarity displayed throughout the various series treated of, together with the number of oxygen atoms relative to the number of carbon atoms, and the almost certain positions taken up by those oxygen atoms in the molecules of lesser magnitude, enables one to treat as proofs what might otherwise be justly treated as analogies in dealing with those molecules of higher magnitude. For example, there is no doubt whatever but that two thymol molecules are condensed to a dithymol molecule as one result of the reaction, and from this we may assume the same to be true in those cases where actual coalescence, attended with elimination of carbon, of two contiguous molecules also takes place at one stage or another.

In representing the products from simple phenol, the iodine atoms have been placed vertically opposite without any proved reason for doing so. At least one of the iodine atoms must occupy the position in the benzene ring usually denoted by the cipher 4, whilst the second iodine atom might be supposed to be attached at positions 1 or 2.

There can be little doubt but that the positions actually taken up are the same as those occupied by the iodine atoms of the true di-iodophenol obtained at the same elevation of temperature under otherwise different conditions; and it may also be safely assumed that such true substituted phenol is, in general, primarily formed. However, the relative positions of the substituted iodine atoms of this particular di-iodophenol are not at present known, so that the information cannot be derived from this source.

In the ordinary, and what may perhaps be called the normal, product obtained from thymol, that is, the compounds which contain a dithymol molecule, the iodine atoms are represented as being attached to the carbon atoms of positions 6 in each ring. Those positions would almost naturally suggest themselves as being the most likely. Messinger and Vortman adjudicated those positions to the iodine atoms, because the red compounds could be prepared from Willgerodt's iodothymol, in which the iodine atoms are recognised as occupying such positions. This affords no proof whatever that the red compounds hold the iodine atoms in any particular position, except in such special cases where they are actually prepared from this particular iodothymol, because the formation of the red compounds is not a consequence of the true substituted iodine atoms occupying any particular positions; indeed, there is no reason why such red compounds should not be possible of formation without their containing any true substituted iodine whatever. True substitution by iodine must be looked upon as merely a consequence of the necessary method of manipulation and concurrent conditions existing, putting aside all con-

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* In these determinations of furfural the method of volumetric estimation (Gunther and Tollens) was employed. After the publication of the latest communication on this subject (Flint and Tollens, *Landw. Vers. Stat.*, 1893, xlii., 381—407), the determinations were repeated on the gravimetric plan, *i.e.*, of weighing the hydrazone. Identical results were obtained.

† Traces only of gaseous products are formed in these oxidations.

siderations as to accelerating physical influences induced as the result of substituting an atom of iodine in the molecule.

It will be observed that in those cases where coalescence of two benzene nuclei also takes place, the iodine atoms are represented in position 2 of the ring as a necessary consequence, without assuming attachment to oxidised carbon atoms or to oxygen atoms direct.

Messinger and Vortman represent the hypothetical third iodine atom of the condensed molecule as being directly attached to an oxygen atom, but I have shown that the compounds contain no such third iodine atom. This idea seems, however, to have taken possession of various authors, for we now fine aristol represented as containing both iodine atoms attached directly to the oxygen of the hydroxyl groups without any apparent reason for doing so, and on that account called an iodide.

However, there would be nothing improbable in the compounds containing an oxy-iodine group in the ordinary places of substitution taken up by the simple iodine atoms, and, indeed, the number of oxygen atoms found in the compounds suggest distribution as such.

In order to prove or disprove this possibility a considerable quantity of the product from phenol and also one of the products from thymol were fused up with potash, but no such oxy-iodine radicle could be separated, and on that account the oxygen atoms throughout the foregoing paper have been represented as occupying the positions originally occupied by the hydroxyl groups. In doing so it has been assumed that if addition of oxygen took place it would most likely take place where oxygen already existed, the hydrogen of the hydroxyl being in general eliminated. The analytical data agree with this assumption; still it is not a little remarkable when we consider that other carbon atoms are simultaneously removed together. There is no reason why the iodine atom may not be united directly to the carbon atom also united to oxygen.

Too much stress should not be placed on the percentage of hydrogen shown by analysis, since this was generally regarded as a matter of secondary importance, and a slight difference in time of manipulation is capable of making a difference of 0·2 per cent, which indicates a considerable difference on calculating into atoms.

### *The "Encluded" Iodine.*

The true substituted phenols are not capable of "encluding" iodine either at the moment of formation or by subsequent manipulation. It cannot be imagined that such a molecule oxidised would; indeed, I have shown in a special case that it does not (see *ante*). What, then, can be the cause of such "enclusion" if not molecular condensation?

On reviewing the constitutional representations of the molecules dealt with from this standpoint, one may be struck with the peculiar suitability for such "enclusion" by virtue of the relatively large vacant space which must exist around the points of condensation; and assuming the representations to be fundamentally true, this suitability may be considered largely increased by virtue of such vacant space being a closed one, and therefore admirably fitted to "enclude" matter presented in a sufficiently fine state of sub-division. Then, again, there is the mere mass attraction, consequent upon the individual masses of the opposite rings of the molecule. Moreover, the angles of attraction at the points of condensation may be regarded as abrupt. Abrupt angles and terminations are, generally speaking, abnormal natural products—at all events, in complex structures. May it not be that the iodine in this case arches the corners, so to speak? May not chemical spheroidicity play an important part in chemical constitution?

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**Statue to the late M. Chevreul.**—A bronze statue of the late illustrious chemist Chevreul has been erected at his native town, Aggerz.

## RECENT ADVANCES IN AGRICULTURAL CHEMISTRY.

It has been repeatedly observed that if some one introduces into commerce a new toy, or a new game, or a new quackery, he will probably reap a golden harvest; but if he devises some great, decisive improvement in one of the most important arts, his reward will be neglect and opposition. Such has been the lot of M. Georges Ville. He has spent years and large sums of money in the improvement of agriculture. He has studied the action and the economy of manures, and has brought his conclusions to the test of experiment on a practical scale and with uniform success. The land-owners and farmers who have carried out the suggestions of M. Ville have had no reason to repent. The scientific and technical press has given him very generally its support. His works have had a wide circulation. Still the great mass of farmers hold aloof, and persist in following the routine which their forefathers used in the last century, which is no longer able to meet the conditions of the present day.

M. Ville seeks to convince the farmer that to keep cattle as producers of manure is a capital error. Such manure, if carefully valued, is found to cost more than its actual worth, and much more than the cost of an artificial manure of equal or superior value. Farm-yard manure is found to contain only 1·48 per cent of plant-food; it has the defect that its composition cannot be varied according to the requirements of any particular crop. Now, with farm-yard manure no such adaptation is possible. Further, if a pasture-land is poor in phosphates, the excreta of cattle fed upon it cannot be rich in phosphates, and will be very ill-adapted as a fertiliser for any crop which is in need of phosphoric acid.

In one of his works ("La Betterave et la Legislation des Sucres") M. Ville cautions his readers against the use of the Stassfurth potash salts. He contends that night-soil, at least if applied to the sugar-beet, yields very heavy crops, but at the expense of the quality of the roots, which are hollow and poor in sugar. He places the sources of nitrogen in the following ascending series as regards their efficacy:—Organic nitrogen, ammonium sulphate, sodium nitrate, and potassium nitrate. He insists, very justly, on the maintenance of a due equilibrium among the constituents of plant-food; if any one of these ingredients is in excess, the surplus contributes neither to the quantity nor to the quality of the crop, but remains in the soil without being taken up by the plants, and is consequently wasted as far as the farmer's returns are concerned.

M. Ville's conclusions agree in the main with those of the leading agricultural chemists in this country; but there is one important difference. He classes lime as one of the four constituents with which soils—without distinction of their character—are not provided by nature to an extent sufficient for the growth of plants. Hence it figures in all his formulæ in the state of calcium sulphate, gypsum. Now, in England, experience has shown that—except for certain special crops, such as clover—gypsum is of no appreciable value. Hence plants have been divided into calciphilous and calcifugous. The former grow by preference naturally in calcareous earth, and when growing in ordinary average soils are distinctly benefitted by dressings of lime or of manures containing lime. The calcifugous plants, on the contrary, may be exterminated by the application of lime. If we consider that the proportion of calcareous matter in soils capable of cultivation may exceed 30 per cent, we may be surprised when told that lime is universally necessary, as are nitrogenous matter, phosphoric acid, and potash. It may be said, in reply, that lime in the state of carbonate is insoluble in water, and thus is not available as plant-food. But it does dissolve in water charged with carbonic acid, and this is the condition generally occurring in the soil.

M. Ville has made a series of experiments by adding to a soil "complete manure," *i.e.*, nitrogenous matter, phosphate, potash, and gypsum, and has obtained a crop of 51,000 kilos. On omitting the lime the yield was only 47,000 kilos.; If the potash is omitted it falls to 42,000 kilos.; without phosphate it is merely 37,000, without nitrogenous matter 36,000, and without manure at all 25,000. But we do not see that he has tried the effect of the soil with the addition of lime alone.

The cultivation of beetroot is recommended by the author as a key to the agricultural situation. As a nation we can look upon it with little sympathy. It was one of the weapons used against us by the first Napoleon, and it has wrought us a grave amount of injury.

Before passing on to examine in our next the author's social and economical views, we must notice his assertion that "in cold and misty regions the use of tea predominates over that of coffee, whilst in hot countries coffee has the upper hand." In contradiction to this rule we must point out that in Australia, which is hotter and drier than any European country, the consumption of tea is exceptionally large, whilst in cold Norway coffee is in almost exclusive use.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 201).

They are certainly comparable among themselves, but not with the relations of sensitiveness of the photographic plate. They are this just as little as the behaviour of one kind of plate can be decisive for the behaviour of another kind. Between the ocular and the photographic method of determining the luminosity, in particular of the ultra-violet rays, there is certainly an internal connection, that of absorption; but how little decisive this is for the case in question is best proved by the fact that every substance has its own absorption spectrum. It must be also remarked, in passing, that ocular determinations of luminosity, even when they refer to light of the same quality, afford only a very imperfect guide to the objective luminosity.

It was therefore absolutely necessary to re-examine quartz and gelatin in this respect. In the same manner I was restricted to my own resources in determining the absorptive action of the air.

A medium has still to be considered which is much more important for my proofs than the substances just named—the sensitive constituent of the photographic plate, silver bromide. The success of the photograph depended in the first place on the behaviour of this subtance. If it was in reality so feebly sensitive to the most refrangible rays as my proofs seemed to indicate there then came up the further problem to find a suitable substitute for silver bromide.

The determination of the sensitiveness of silver bromide turned likewise in the first place in an absorption experiment. For it could possess higher sensitiveness only if it absorbed the rays with sufficient energy, preferably in the modification used in photographic dry plates. On the manner of the extinction of the rays, whether photochemic or photo-thermic could be decided only by the photographic behaviour of a silver bromide free from any admixture of foreign constituents. It might appear as if a proof with pure silver bromide would alone suffice for this purpose, and as if a knowledge of the absorption might be dispensed with. But this view is contradicted by certain facts of that part of my preliminary researches concerning the production of a new photographic plate,—of which below.

In this manner I might anticipate better results in the region of the smallest wave-lengths than heretofore, but always with the apprehension that the hoped for rays beyond the limit of activity already reached might indicate a quite different behaviour than those on which my previous experiments were founded. I commenced my preliminary researches with quartz, followed in succession by gelatin, silver bromide, and air.

(To be continued).

## THE ACTION OF AMMONIA GAS UPON MOLYBDENYL CHLORIDE.*

By EDGAR F. SMITH and VICTOR LENHER.

In 1857, Tuttle (*Annalen*, ci., 285) studied the action of ammonia upon molybdenum trioxide and molybdenum chloride ($MoCl_4$). In the case of the trioxide the temperature at which the reaction was made approached a red heat. The resulting product was in part black in colour and possessed metallic lustre. Its analysis revealed the presence of nitrogen, oxygen, hydrogen, and molybdenum. The quantity of the latter constituent equalled 92·9 per cent. Upon conducting the reaction at more elevated temperatures, the product was found to contain 77·9 per cent and 73 per cent of molybdenum, while the hydrogen content did not exceed 0·18 per cent. The results consequently were not constant.

On exposing molybdenum chloride to the action of ammonia gas at a temperature just sufficient to volatilise the ammonium chloride which arose in the reaction, Tuttle obtained a black metallic sintered mass. It was found to contain 82·83 per cent of molybdenum, and was assumed to have the composition expressed by the formula $Mo_2N_2 + Mo(NH_2)_2$, analogous to a compound of tungsten obtained in a similar manner by Wöhler (*Annalen*, lxxiii., 190).

Several years after the publication of the preceding investigation, Uhrlaub presented an inaugural thesis entitled "Die Verbindungen einiger Metalle mit Stickstoff" (Goettingen, 1859), from which we collate the following interesting facts:—

In the action of ammonia gas in the cold upon molybdenum chloride much heat was evolved and a black coloured product resulted; its analysis showed the presence of 76·457 per cent of molybdenum, 23·134 per cent of nitrogen, and 0·677 per cent of hydrogen. In subsequent experiment Uhrlaub employed a more intense heat, thus hoping to eliminate the slightest hydrogen content, but this element continued to show itself in his various products, until on raising the tube in which the reaction took place to an intense red heat he obtained a compound that careful analysis gave a composition which may be expressed by the formula $Mo_3N_2$. In other words, a molybdenum nitride had been formed by acting upon the chloride of the metal with ammonia gas at a high temperature.

When Uhrlaub tried the action of ammonia upon molybdic acid at a gentle heat, he obtained "pseudo-morphuen," as he designated them, bluish black in colour. Several were prepared; they varied much in composition. Uhrlaub attributes this variation to the different degrees of heat employed and to the length of time during which the heated molybdenum trioxide was exposed to the action of the gas.

The preceding facts indicate that the action of ammonia gas, either upon the trioxide or chloride, is not as simple as might be presumed. An amide that might well be ex-

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

* Read before the Chemical Section of the Franklin Institute, May 16th, 1893.

pected in either case appears not to have been obtained by either Tuttle or Uhrlaub.[*]

We hope to reach this result by the action of ammonia gas upon molybdenyl chloride, in accordance with the equation—

$$MoO_2Cl_2+4NH_3=MoO_2(NH_2)_2+2NH_4Cl.$$

It will be noticed that we apply the term molybdenyl chloride to the compound generally called molybdenum dioxychloride. Our assumption of molybdenyl is based upon the terms sulphuryl, chromyl, &c., applied to compounds possessing a constitution similar to that of the dioxychloride of molybdenum, $MoO_2Cl_2, SO_2Cl_2, CrO_2Cl_2$.

*Preparation of Molybdenyl Chloride.*—Of the various methods proposed for the formation of this derivative of molybdenum, we discovered that the action of dry chlorine upon the dioxide of the metal yielded by far the most satisfactory product, both as to purity and quantity.

At a very gentle heat the molybdenyl chloride forms rapidly and sublimes in feathery crystals. Schulze (*Journ. Prakt. Chemie*, xxix., N. F., p. 440), in discussing the action of molybdic acid upon metallic chlorides, proposes this procedure for the object we had in view, but we failed to meet with success in our applications of the method. The yield was not very abundant.

The crystalline molybdenyl chloride, prepared as described, was introduced into porcelain boats, and these placed in tubes of hard glass, through which we conducted a brisk current of well dried ammonia gas. The molydenyl chloride immediately assumed a deep black colour, much heat was evolved, and copious fumes of ammonium chloride vapour were carried out of the tube. Considerable moisture also collected upon the anterior portion of the combustion tube. At last heat sufficient to expel any ammonium chloride retained by the compound was applied; but it was not for a longer period than half an hour. The boat and contents were cooled in ammonia gas. The product of the reaction was placed over sulphuric acid to absorb any retained gas; a portion of it was also washed with water, and the aqueous solution examined for chlorine, but this was not found present. In general appearance the product was metallic and black in colour. Analyses were made of different preparations. The molybdenum content was determined by oxidising weighed portions of material with dilute nitric acid, evaporating carefully to dryness, finally applying a gentle heat for a period of fifteen minutes.

The hydrogen was estimated by burning the material in a current of oxygen, and collecting the water that was produced in a weighed calcium chloride tube.

The nitrogen estimations were three in number; one of them was carried out by the method of Dumas, while the other two were made by the soda-lime process.

The oxygen was obtained by difference.

Our analytical results may be tabulated as follows:—

*Molybdenum Determination.*

| | | $MoO_3$ found. Grm. | | Mo. Per cent. |
|---|---|---|---|---|
| 1. | 0·1047 grm. substance taken | 0·1156 | = | 73·65 |
| 2. | 0·1006 " " | 0·1108 | = | 73·42 |
| 3. | 0·1004 " " | 0·1110 | = | 73·70 |
| 4. | 0·1028 " " | 0·1113 | = | 73·47 |
| 5. | 0·1017 " " | 0·1126 | = | 73·80 |

The mean molybdenum percentage of these five determinations is 73·61 per cent.

*Hydrogen Determination.*

| | Water found. Grm. | | H. Per cent. |
|---|---|---|---|
| 0·2088 grm. substance taken .. | 0·0082 | = | 0·43 |

*Nitrogen Determination.*

| | | Pt found. Grms. | | N. Per cent. |
|---|---|---|---|---|
| 1. | 0·1510 grm. substance taken | 0·0643 | = | 6·05 |
| 2. | 0·1529 " " | 0·0642 | = | 5·96 |

The nitrogen found by the Dumas method equalled 6·00 per cent, and the mean of the three nitrogen estimations was also 6·00 per cent.

Two-thirds of this nitrogen content were expelled when our compound was exposed to the action of hydrogen at the highest temperature attainable with a good combustion furnace.

Taking the mean of our analysis as a basis of calculation:—

| | Per cent. |
|---|---|
| Mo.. .. .. .. .. .. | 73·60 |
| N .. .. .. .. .. .. | 6·00 |
| H .. .. .. .. .. .. | 0·43 |
| O (by difference).. .. | 19·96 |

we deduce $Mo_5O_8N_3H_3$ as the most probable empirical formula, which may be variously written to express the enigmatical constitution of this compound. Thus it might be $MoO(NH)_2.MoONH.3MoO_2$, or—

$$4MoO_2.Mo(NH)_3,$$

which may be correctly termed tetramolybdenyl molybdenimide.

Our compound is stable in the air. Hydrochloric acid does not affect it. Nitric acid of sp. gr. 1·42 causes it to burn very energetically. Dilute alkalis attack it very sluggishly. It liberates ammonia when fused with caustic potash. When heated in a current of oxygen it is slowly oxidised. Heated in nitrogen gas, the black compound loses water and assumes a reddish colour. An analysis of this product indicates that it was probably molybdenum dioxide mixed with a very small amount of nitride; at least, traces of nitrogen were found upon examination. Another interesting observation was that when the black product was introduced into an aqueous solution of silver nitrate, crystals of metallic silver gradually appeared over the surface of the molybdenum compound.

We obtained our first product several times, but care must be exercised and the same conditions noted by us strictly observed if success in its formation is desired.

An examination of Uhrlaub's analytical results will show that one of his products approaches very closely the compound we have just described. He speaks of it as a black "pseudomorph" with the composition—

| | | |
|---|---|---|
| Mo .. .. .. .. .. | 73·55 | per cent. |
| N .. .. .. .. .. .. | 5·58 | " |
| H .. .. .. .. .. .. | 0·54 | " |
| O .. .. .. .. .. .. | 20·30 | " |

The formula deducted from these figures differs from that presented by us, and what is more, if we understand Uhrlaub correctly, his compounds prepared from ammonia gas and molybdenum trioxide were all "blau-schwarz" in colour, and were not acted upon in the cold by nitric acid (see his "Dissertation," pp. 13, 14, 17).

However, it is evident that the product we obtained by the action of ammonia gas upon molybdenyl chloride is not the amide we had in view. Thinking that perhaps the heat we applied to drive out the final traces of occluded ammonium chloride may have been sufficient to alter the composition of the product formed at first, we allowed the ammonia to act upon the molybdenyl chloride at the ordinary temperature, and when there was no further evolution of ammonium chloride and the boat had become perfectly cold,[*] we introduced carbon dioxide, applying a very gentle heat at the same time,

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[*] The primary object of these gentlemen seems to have been the preparation of molybdenum nitrides.

[*] Portions of the product removed at this stage and shaken with cold water decomposed into a mixture of blue- and brown-coloured masses. The possibility of removing the ammonium chloride was, therefore, excluded.

but we failed to achieve our aim. Nitrogen, when substituted for carbon dioxide, gave us no better result. We next dissolved molybdenyl chloride in the purest ether we could get, and conducted ammonia gas into this solution. We obtained decomposition products. A closer examination of the behaviour of the molybdenyl chloride towards ether revealed the fact that the moment the two came in contact a slight hissing sound was perceptible, and the ether at once imparted a strong acid reaction to blue litmus. The same was observed when pure chloroform was employed as a solvent.

If molybdenyl chloride be gradually heated in an ammonia atmosphere until the tube of hard glass becomes bright red in colour, and the gas action be continued for an hour, the resulting product will be an amorphous metallic black mass. Subjected to analysis it gave results as appended.

*Molybdenum Determination.*

| | $MoO_3$ found. | Mo per cent. |
|---|---|---|
| (1) 0·1042 grm. substance taken .. | 0·1061 grm. = | 67·87 |

*Nitrogen Determination.*

0·1025 grm. substance burned with soda-lime gave 7·00 per cent N.

*Hydrogen Determination.*

0·1012 substance ignited in a current of oxygen gave 0·0109 grm. of water equal to 1·19 per cent H.

| | | |
|---|---|---|
| Mo .. .. .. .. | 67·87 | per cent. |
| N .. .. .. .. .. | 7·00 | ,, |
| H .. .. .. .. .. | 1·19 | ,, |
| O (by difference) .. | 23·94 | ,, |

The empirical formula deduced from these figures is $Mo_7O_{14}N_5H_{10}$, which can also be written—

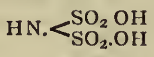
$$4MoO_2.2MoO_2(NH_2)_2.MoO_2NH_2.$$

Dilute alkalies have no effect upon this compound; but it liberates ammonia when fused with caustic potash. It is converted into molybdenum trioxide very energetically —with evolution of sparks—when brought in contact with cold nitric acid.

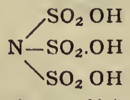
Other products were obtained by us; their analyses lead us to the conclusion that with us, as with Uhrlaub, the composition of the derivative depended wholly upon the length of time during which the gas acted upon the molybdenyl chloride, and the degree of heat employed in the experiment. It seems highly improbable to us that the amide $MoO_2(NH_2)_2$—molybdenyl amide—can be prepared after the fashion pursued by us, for it is quite certain that the heat of the reaction evolved in the first contact of the ammonia with the molybdenyl chloride exercises a very potent influence upon the composition of the product.

When we recall the action of ammonia gas upon sulphur trioxide and sulphuryl hydroxy-chloride resulting in the compounds with the following constitution—

$$H_2N.SO_2OH$$



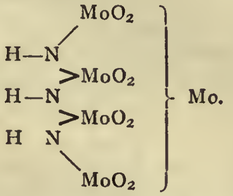
$$HN.<\begin{matrix}SO_2\,OH\\SO_2.OH\end{matrix}$$



$$N\begin{matrix}\diagup SO_2\,OH\\ -SO_2.OH\\ \diagdown SO_2\,OH\end{matrix}$$

the question that obtrudes itself is: Are not these products and their methods of formation types of the processes and results that have occurred not only in our studies described in this paper, but also in the studies of Tuttle and Uhrlaub?* Are not their products, as well as our own, only residues of amide, imido, and nitrito molybdic acids?

Above we have written for our first product the constitutional formulæ $MoO(NH)_2.MoONH.3MoO_2$, and $4MoO_2.Mo(NH)_3$, but after considering the sulphur types we would express our empirical formula $Mo_5O_8N_3H_3$ differently, as follows:—



We have here several broken-down molybdenyl amide nuclei in conjunction, not chemically combined, with metallic molybdenum. Reviewing the behaviour of the product which we thus graphically represent, we may be allowed to emphasize the fact that when it was brought in contact with an aqueous argentic nitrate solution, metallic silver was precipitated, and this we know from Smith's (*Zeit. für Anorg. Chemie*, i., 360) observation is a property of metallic molybdenum. Further, it will be recalled that when our product was heated in an atmosphere of nitrogen it left a reddish coloured compound, which upon analysis approximated the requirements of molybdenum dioxide, and that traces of nitrogen were also detected in it. All these experimental facts find expression in our graphic representation above.

The second product obtained by us was even more active when introduced into a silver nitrate solution, throwing out metal quite rapidly, proving in our opinion the presence in it of even a greater quantity of metallic molybdenum than is contained in the first body. Similar reduced molybdenyl amide nuclei mixed with metallic molybdenum, could also be constructed for our second compound, and be in harmony with the observed deportment of this body if it were necessary.

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## IMPROVED PROCESS FOR THE RAPID AND CERTAIN DETECTION OF CHOLERA BACILLI.

By R. KOCH.

This process, according to the author, if suitably applied, indicates even single cholera microbia in drinking-water and river water. The method requires that, whilst observing the well-known precautions, a little of the suspected water is added to a solution of peptone and allowed to stand at 37°. If there are in the material only very few cholera bacilli capable of development, they increase very remarkably at the above temperature in from six to twelve hours. In consequence of their avidity for oxygen, they collect upon the surface of the liquid, where, under certain circumstances, they form a fine film, distinctly visible. On the microscopic examination of a drop of the liquid from the surface, the characteristic "comma bacilli" are seen in prodigious numbers.

In order to be quite certain in the diagnosis, we take a drop from the surface of the liquid containing the bacilli and make up gelatin—or, preferably, agar—plates according to the old method. If the gelatin plates are allowed to remain at 22° (or the agar plates at 37°), in from ten to fifteen hours the cholera bacilli (if present) will have grown to characteristic colonies, so that in the most difficult case a demonstration can be secured within about from twenty-one to twenty-seven hours.—*Zeit. für Hygiene* and *Zeit. Anal. Chemie.*

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**Mr. F. G. Adair Roberts**, partner in the well-known firm of Boake, Roberts, and Co., Stratford, London, has just been elected to a seat on the West Ham Town Council. We understand his election gives general satisfaction to his fellow townsmen.

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* At least in so far as the action of ammonia gas upon molybdenum trioxide was concerned.

## COLOUR REACTIONS OF CERTAIN AROMATIC TRIOXIDE COMPOUNDS.

By J. STAHL.

THE reactions mentioned occur in the cases of pyrogallol, gallic acid, pyrogallocarbonic acid, and tannin. In all these substances alkalies, with the simultaneous action of the oxygen of the air, produce brown or brownish red colours, even if the trioxy-compounds are present only in very minute quantities.

1-1000th m.grm. of pyrogallol gives the reaction with ammonia, and soda-lye with 5-1000th m.grm.; 2-1000th m.grm. gallic acid and tannin and 1-100th m.grm. pyrogallocarbonic acid yield the reactions.

In a series of other reactions given for the trioxy-compounds, *e.g.*, potassium cyanide, sodium nitroprusside, arseniates, &c., the author ascribes the result to the alkalinity of the reagents, the other components merely producing slight modifications in the colour.

Baryta- and lime-water give the above named trioxide compounds the same colour reactions as the true alkalies. Other phenols give with the alkaline earths yellow or reddish tones (resorcine, hydroquinone, phloroglucine) or no colourations (α-naphthol, thymol, paracresol). β-naphthol turns bluish; pyrocatechine, first violet, afterwards greenish black.

As regards the reactions—none of them characteristic—produced by osmic acid, molybdic acid, and solutions of chloride of lime, as also by the oxides of nitrogen and the compounds of chromic acid, we must refer to the original.

The behaviour of the trioxy-compounds with the compounds of iron is characteristic. Pyrogallocarbonic acid yields with concentrated solution of ferric chloride a greenish brown colouration or, if much diluted, a violet.

The most sensitive reaction for pyrogallol (5-1000th m.grm.) is a mixture of ferric chloride and potassium ferricyanide, which in consequence of the reduction of the ferric chloride to the ferrous state gives a precipitate of Turnbull's blue. Gallic acid, in the absence of air, is not affected by ferrous sulphate.—*Zeit. Anal. Chemie* and *Pharm. Central Halle.*

# PROCEEDINGS OF SOCIETIES.

## ROYAL INSTITUTION OF GREAT BRITAIN.

*General Monthly Meeting, Monday, November* 6, 1893.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Society:—John Astley Bloxam, F.R.C.S., Matthew Wilks Geary, F.R.G.S., James Sidney Hargrove, Gordon Donaldson Peters, Jean Paul Richter, Ph.D., Sir Richard Henry Wyatt, D.L., J.P.

The Managers reported, That at their meeting held this day they had elected Charles Stuart, M.R.C.S., Fullerian Professor of Physiology for three years (the appointment dating from January 13, 1894).

The special thanks of the Members were returned to Lord Armstrong for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

# NOTICES OF BOOKS.

*Agricultural Analysis: a* Manual of Quantitative Analysis for Students of Agriculture. By FRANK T. ADDYMAN, B.Sc., F.I.C. London: Longmans, Green, and Co. 1893. Small 8vo., pp. 200.

THE first part of this useful Manual treats of the appliances and manipulations used in quantitative operations. It is to be regretted that a somewhat pedantic feeling has led the makers of French weights to adopt and cling to the divisions 0·3, 0·2, 0·1. Any one who takes the trouble to compare will find that any given weight can be made up more conveniently with touching a smaller number of pieces on the English division 0·6, 0·3, 0·2, 0·1. In like manner the French flat plates are much less convenient than bent wires. If these two little points could be attended to the advantages of the metric system would be at once recognised.

Part II. gives directions for determinations, gravimetric and volumetric, the latter section including the preparation of standard solutions and the selection of indicators.

Part III. is devoted to the determination of nitrogen. Here we note a curious slip of the pen. The soda-lime process is mentioned as due to Dumas, instead of to Will and Varrentrap. The Kjeldahl process, or rather its modification as devised by Dunning, is admitted as preferable in a number of cases, especially where very many determinations have to be conducted.

For the expeditious determination of nitrogen in nitrates the Ulsch method is recommended. Lunge's nitrometer method is also described, and the apparatus is figured.

In Part IV. instructions are given for sampling, a subject too much neglected, and productive of unedifying disputes between seller, buyer, and analyst.

In Part V. we find directions for the analysis of feeding materials, whilst Parts VI. and VII. are devoted respectively to the analysis of manures and soils. In determining phosphoric acid the magnesia process is given, and, where iron and aluminium are present, the molybdic method. The treatment of fish manure, the excreta of bats, &c., are specially described, with the caution that in all fish guanos oil must not be present in quantities exceeding 3 per cent. Night-soils, sewage-manures, and blood-manures are not specially mentioned. Instructions are given for the analysis of gas-lime.

The directions for the analysis of milk, butter, and cheese are somewhat brief. A caution is, however, given as to the possible presence in cheese of margarine and of lead chromate.

For the analysis of drinking-waters the Wanklyn process is given, with the addition of Hehner's method of estimating hardness. The necessity, in certain possible cases, of a bacteriological examination of waters and milks is not taken into consideration, probably as the necessary information is to be found in several recent works.

Throughout the book the author has kept his eye on "South Kensington," but he has not appended any lists of questions set at any "exam." His instructions are so clear and judicious that students will find the work a trustworthy guide.

*Measurement of Light in Colour Sensations.* A New Method of Investigating the Phenomena of Light and Colour by means of the Selective Absorption in Coloured Glass, Graded into Scales of Equivalent Colour Value. By JOSEPH W. LOVIBOND, F.R.M.S., The Colour Laboratories, Salisbury. London: G. Gill and Sons.

THE main object of the present work is to describe the structure and the applications of a most useful instrument which has been devised by the author, and which is, we hope, coming more and more into use. Not a few arrangements have been proposed for estimating and recording the exact tones and intensities of colours. We may mention the colorimeters of Dubosq, Stanmer, Wolff, Fleische, &c. None of these, however, are fully satisfactory, and we may therefore congratulate Mr. Lovibond on the invention of his *tintometer*, which obviates most of the defects of the instruments previously in use. The peculiarities of the tintometer include the use of graded coloured glasses as standards of comparison instead of solutions, of appliances for excluding side-light, and for giving a direct view without the use of lenses, prisms, or reflectors. In addition to the instrument itself, the tintometer, the author puts forth as novelties in his system the glass colour scales and the colour equivalence of their several units, his scheme of notation and colour nomenclature, his system of colour charts, and the determination of the smallest increment of colour appreciable to a trained normal vision. This limit he fixes at 0·006 of a standard colour unit.

On the subject of primary colours he gives an uncertain sound. In addition to the theory of Newton and Chevreul (red, yellow, and blue), and that of Young and Helmholtz (red, green, and violet), he mentions a 4-, a 5-, a 6-, and a 7-ray theory, but he accepts "as the three primaries, in the original sense of the word," orange, green, and violet. He limits the number of separate colour sensations to twelve, six of which are simple and six compound. Like all practical men, he advises that diffused day-light, preferably from the north, should be used for examining and comparing colours, and he insists in all cases upon an equality of light in both tubes of the instrument.

Mr. Lovibond's method of measuring colour in the spectrum of diffused daylight depends on progressive absorption. He intercepts the spectrum of the light with glasses of a neutral tint until the weakest colour-ray is absorbed, then adding the necessary glasses until the next weakest, and so on until all are absorbed.

A description of the tintometer without the accompaniment of diagrams would be of little value. But it is our very agreeable duty to call attention to some of the practical applications which the tintometer has already received. Thus, Prof. Munro has worked out the tintometer measurement of ammonia in water and distillates under different conditions, taking into account the age of the Nessler solution and the time in which it is left in contact with the liquid under examination. The influence of the temperature of the solution has subsequently been studied by Messrs. Hazen and Clark (Chemical News, vol. lxii., p., 125).

Mr. T. Jobson has applied the instrument for estimating lead in waters. The analytical method is the same which has been established by W. A. Miller and J. A. Wanklyn, but the tintometer comes in to measure the depth of colour produced.

H. Le Neve Foster has found Mr. Lovibond's instrument most useful in the analysis of steels by the Eggertz colour method, or by Stead's colour method.

The tintometer is useful also, according to Mr. Sanderson, the secretary of the Association of British and Irish Millers, for measuring or reproducing the colour of any given sample of flour.

Use has already been made of colour in judging of the presence and proportion of organic impurities in drinking-water, reservoirs, rivers, sewage, and effluents. But the tintometer enables such observations to be made with more ease and with numerical accuracy.

In a variety of other cases the tintometer must also prove valuable. It will in many cases relieve the dyer and colour manufacturer from the necessity of depending entirely on swatch-dyeing, as well in their materials as in their finished products. The paper-maker can by means of this instrument examine his water, his half-stuff, and his bleached pulps. The wine-grower and distiller will find this instrument advantageous.

Mr. Boverton Redwood, in conjunction with the author, has examined by this means petroleum, shale, and cocoa-nut oils. But, perhaps, the most widely reaching application of Mr. Lovibond's instrument is in the study and detection of colour-blindness. In this department the author has enjoyed the co-operation of Mr. Priestley Smith, of Birmingham, who has suggested some improvements in the instrument for this especial purpose. It is incidentally remarked that some of the standard wools of Holmgren's system fade considerably, and should be periodically verified.

The tintometer can be applied, not merely for examining liquids, but also for solids and pigments, and there is little doubt but that its uses will meet with rapid extension. Those who give the instrument a careful trial, whether in pure research—chemical, physical, or biological—or in practical operations, will find occasion to be satisfied with the results.

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*The Chemistry of Fire.* By Pattison Muir, M.A., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Methuen and Co. 1893. Crown 8vo., pp. 163.

This little work, which belongs to the University Extension Series, is edited by J. E. Symes, Principal of University College, Nottingham. The author is already favourably known to most of our readers from his writings on questions in the philosophy of chemistry. In the present work Mr. Muir expounds the elementary principles of chemistry from the well-known facts of combustion, taking the case of a candle. He remarks that "to understand the occurrences included in the every-day process of burning a candle is to understand the whole of chemistry and no small part of physics." To the thoughtful reader, who is seeking to *know* and not to "*pass*," this book will prove a suggestive guide.

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*A Guide to the Examination of the Urine.* By J. Wickham Legg, Fellow of the Royal College of Physicians of London, formerly Assistant Physician to St. Bartholomew's Hospital, and Lecturer on Pathological Anatomy in the Medical School. Seventh Edition. Edited by H. Lewis Jones, M.A., M.D. London: H. K. Lewis. 1893. Fcap. 8vo., pp. 139.

The examination of urine as a clue to the condition of health has been in use for centuries by herbalists, astrologers, wise women, village sages, and all manner of quacks. These worthies, if we may believe Shakspere, knew how to give responses as ambiguous as those of the Delphian oracle. Said the doctor whom Falstaff consulted: "The water itself was a good healthy water, but for the party that owned it he might have more diseases than he knew for." But now urinoscopy has passed into the hands of qualified physicians who have at command the resources of chemical and physical science, the results obtained are of the utmost value.

The author of the work before us gives a table of the average composition of the urine, with its daily quantity. There follows a general preliminary scheme for the examination of urine, first physically and then chemically. In searching for albumen, the coagulation by means of picric acid is duly recognised as a valuable test. For the detection of sugar, the methods of Moore, Trommer, and Fehling are described, as also the fermentation process, the indigo-extract test, the picric acid and the phenylhydrazin tests. The question whether normal urine contains sugar is considered still undecided. For the recognition of blood, the spectroscopic detection of the absorption bands of hæmoglobine is recommended. The indications of the guaicum test are regarded as indecisive, unless confirmed by other reactions. For the recognition of some of the urinary pigments, such as urobiline, uroerythrine, and hæmatoporphyrine, the spectroscope useful.

Throughout the book cautions are given concerning errors which may possibly arise from the presence of unusual and unsuspected substances. The illustrations are excellent, especially the photographic reproductions of specimens of urinary crystals. But there is little need to express further approval of a work which has reached its seventh edition.

*Inorganic Chemistry for Beginners.* By Sir **Henry Roscoe**, F.R.S., D.C.L., LL.D., assisted by **Joseph Lunt**, B.Sc., F.C.S. London: Macmillan and Co. 1893. Small 8vo., pp. 245, with 108 Illustrations in the Text.

The publishers, says the author, have called his attention "to the want of a work for those beginning the study of the science in which the elementary principles of chemistry are more fully treated than is the case" in his "Elementary Lessons in Chemistry." We cannot for a moment question the judgment of Messrs. Macmillan in their own business, though we have certainly been for years of opinion that every type of book which beginners in chemistry might require has been produced in superabundance.

The author describes merely the non-metallic elements, and among those only oxygen, hydrogen, nitrogen, chlorine, sulphur, and carbon, with their more important compounds. The lessons which may be drawn from the study of these substances are very clearly developed.

The book will be excellent for the beginner, though we cannot commit ourselves to the assertion that it has any well-marked advantages over the elementary treatises which are already known.

## CORRESPONDENCE.

### EASY RULE FOR CONVERTING THERMOMETRICAL DEGREES.

*To the Editor of the Chemical News.*

Sir,—I think many of your readers will be interested in the appended rule for the mutual conversion of degrees Centigrade and Fahrenheit, which I devised many years ago for simplifying the usual method of calculation as given in various technical manuals, the latter being cumbrous and not quickly performed, except by an expert reckoner. Almost anyone can readily make the conversion by the new rule without even needing paper and pencil. Such a method might be expected to have been published before, but I have not seen it, nor has anyone to whom I have imparted it.

To reduce a given number of degrees Centigrade to Fahrenheit—
*Rule.*—Double the number and subtract one-tenth of the result.

Fahrenheit to Centigrade—
*Rule.*—Increase the number by its ninth part and halve the result.

The necessary subtraction or addition of 32 at the proper stage is performed in the usual manner.—I am, &c.,

G. Watmough Webster.

Chester, November 1, 1893.

### BARIUM SULPHATE IN SANDSTONE.

*To the Editor of the Chemical News.*

Sir,—In reply to Prof. Clowes's enquiry, I may just say that the barium sulphate occurs to a small extent in the cementing material of the grit as well as in the crevices or joints. I need not further trespass on your space, but will forward a portion of a sample I have to Prof. Clowes with more particulars.—I am, &c.,

H. T. Mannington.

Flint, November 1, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 17, October 23, 1893.

**Analysis of a Vanadiferous Coal.**—A. Mourlot.—The author, referring to a paper by J. J. Kyle which appeared in the Chemical News of October 28, 1892, on the "Composition of a Vanadiferous Coal from San Raphael, in the Province of Mendoza, La Plata," gives an account of a similar coal which he has received from M. Haeren, but for which he gives no locality. The sample is especially interesting as containing in its ash a large proportion of vanadic acid in the state of alkaline and metallic vanadiates. The ash forms 0·63 per cent of the coal, and contains 38·5 per cent of vanadium, or 0·24 per cent as calculated upon the entire coal.

**Perfume of the Violet.**—F. Tiemann and P. Krüger.—The perfume of the violet is obtained either from the fresh flowers of the plant or from the dried root of the iris. The odoriferous principle is a ketone, which the author names irone, and which has the composition $C_{13}H_{26}O$. On submitting to distillation in a strong current of steam the extract obtained by exhausting iris root with ether, we obtain a mixture composed principally of—(1) myristic acid, oleic acid, and other fatty acids; (2) the methylic ethers of these acids; (3) traces of oleic aldehyd; (4) certain neutral substances in minute traces; (5) irone. Irone is an oil readily soluble in alcohol, ether, chloroform, &c. It boils at 144°, its specific gravity is 0·939, and its index of refraction = 1·50113.

**New Synthesis of Erythrite, and Synthesis of an Isomeric Erythrite.**—The author's results show that he has effected the synthesis of a new erythrite, presenting the same structure of atoms of carbon as ordinary erythrite.

**Influence of Organic Solvents upon Rotatory Power.**—P. Freundler.—The totality of these observations seem to demonstrate better than it has been done previously the considerable influence exerted by solvents. Many of the anomalies of the rotatory power of dissolved substances depend on two causes: (1) the polymerisation of the native molecule in solution; (2) the combination of the active substance with the solvent.

**Certain Chemical Conditions of the Action of Beer Yeast.**—J. Effront.—The author studies the action of fluorides upon yeast.

## MEETINGS FOR THE WEEK.

Wednesday, 15th.—Society of Arts, 8. Opening Address, by Sir Richard Webster, Q.C.
Thursday, 16th.—Chemical, 8. "The Normal Butyl, Heptyl, and Octyl Esters of Active Glyceric Acid," by Prof. P. Frankland, F.R.S., and John Macgregor, M.A. "The Ethereal Salts of Diacetyl-glyceric Acid in their relation to Optical Activity," by the same. And other papers.

THE CHEMICAL NEWS.

Vol. LXVIII., No. 1772.

# THE CHEMISTRY OF PLANT FIBRES: CELLULOSES, OXYCELLULOSES, AND LIGNO-CELLULOSES.*

By C. F. CROSS, E. J. BEVAN, and C. BEADLE.

(Concluded from p. 227).

Having now discussed the four constituent groups of the fibre substance, we give the approximate proportions per cent in the annexed diagram:—

$$\underbrace{\underset{60-65}{\text{Cellulose } \alpha} \quad \underset{20-15}{\text{Cellulose } \beta.}}_{\text{Cellulose, } 3.C_6H_{10}O_5.H_2O.} \qquad \underbrace{\underset{18-22}{\text{Complex, } C_{13}H_{16}O_6} \quad \underset{7-9}{\text{Keto-R-hexene deriv.}}}_{\text{Non-cellulose, or lignone, } C_{19}H_{22}O_{10}.}$$

These quantities have been deduced from the foregoing analytical results, and we shall now show that the various determinations taken together are mutually confirmatory, and therefore constitute a satisfactory account in general terms of the jute fibre substance.

*Keto-R-Hexene Constituent.*—The proportion is calculated from the weight of Cl combining with the fibre substance, viz., 7—8 per cent (*Chem. Soc. Journ.*, 1889), and from a study of the attendant results of the reaction (*loc. cit.*). Mairogallol, $C_{18}H_7Cl_{11}O_{10}$, may be considered as derived from a Cl-free molecule $C_{18}H_{18}O_{10}$ [394], which is approximately $3.C_6H_6O_3$, and combines with 11 atoms Cl, *i.e.*, 90 per cent of its weight. Taking the percentage of Cl combining at 7·5 and multiplying by 1·11, we obtain 8 as the approximate percentage of the keto-R-hexene derivative.

*Lignone*, $C_{19}H_{22}O_9$.—The formula of this complex, which is also described as *non-cellulose*, is deduced from that of the chlorinated derivative, $C_{19}H_{18}Cl_4O_9$, by substitution of $H_4$ for $Cl_4$, and may be resolved into the keto-R-hexene group expressed in its simplest terms, $C_6H_6O_3$, and the empirical residue $C_{13}H_{16}O_6$.

The proportion of the formula weight of these groups is 1 : 2·6. If, therefore, the former constitutes 7—9 per cent of the fibre substance, the latter is by calculation 18—23 per cent. Taken together, we may regard the percentage of non-cellulose as 25 by this calculation.

Considering the lignone as an aggregate, $C_{19}H_{22}O_{10}$, we may verify this calculation in the following way:—The carbon contents of $C_{19}H_{22}O_{10}$ is $C = 55·5$. Taking the fibre as an aggregate of 75 per cent cellulose (with 44 per cent carbon), and 25 per cent non-cellulose (with 55·5 per cent C), the carbon percentage of the fibre substance is by calculation—

$$\frac{75 \times 44·0 + 25 \times 55·5}{100} = 46·9.$$

This is entirely in concordance with the results of ultimate analysis, and is further confirmed by the study of the chromic acid oxidation (*supra*). The most noteworthy result of this treatment is the disappearance of the constituent which reacts with chlorine, which appears to be selectively oxidised into soluble products. The loss of weight being 10 per cent, is a further confirmation of the previous estimate of the proportion of this constituent, and the residual fibre, behaving as a mixture of oxidised celluloses, may be regarded as composed of the celluloses $\alpha$ and $\beta$, and the problematical residue, $C_{13}H_{16}O_6$, converted by oxidation (and hydration) into an oxycellulose and yielding furfural with the same facility and approximately in the same quantity as before oxidation.

It must be admitted at this point in the discussion of our results that the deductions therefrom, being in a large measure indirect, are only approximations in regard to the relative proportions of the constituent groups with which we are dealing. Even if the fibre substance were constant in composition, we are limited to the investigation of derivative products, and are still in comparative ignorance as to the mode of union of the parent molecules in the original fibre substance. The fibre substance is, moreover, variable, though within certain limits, which do not appear to be very wide for the fibre produced under normal conditions; but a recent investigation of a specimen produced under "artificial" conditions of growth, has shown that the process of lignification may be made to vary very considerably (A. Pears, *Journal Chemical Soc.*, 1893). Mindful of these considerations, we have drawn our evidence as to composition and constitution from the study of several of the reactions and properties of the fibre substance, *i.e.*, of its constituent groups, each presenting some independent feature of differentiation; and it is in view of the general concordance of the numbers so obtained that the degree of approximation to the truth is to be estimated.

We now have to deal more particularly with the complex represented by the empirical formula $C_{13}H_{16}O_6$. We have explained that this group must be regarded as in union with the keto-R-hexene constituent, and that the union survives the conversion of the latter into the corresponding chloride. The mixed chloride having the formula $C_{19}H_{18}Cl_4O_9$, we regard this as derived from a Cl-free complex, $C_{19}H_{22}O_9$, which we have shown to be decomposable into—

$$\underset{\text{Keto-R-hexene group.}}{C_6H_6O_3} \quad . \quad 2OCH_3 \quad . \quad \underset{\text{Furfural-yielding complex.}}{C_{11}H_{10}O_4.}$$

Respecting the group $C_{11}H_{10}O_4$ we have established the following points:—

It yields, on hydrolysis, 50 per cent of its weight of furfural; it does not combine with the halogens to give substitution products; it is converted by oxidation and hydration (attending liberation from combination) into an oxycellulose, which change to a saturated hydroxy compound may be approximately formulated as under:—

$$C_{11}H_{10}O_4 + O + 5H_2O = C_{11}H_{20}O_{10}.$$

This evidence leaves us no choice but to regard the methoxyl groups as attached to the complex $C_{11}H_{10}O_4$, and even then we cannot be dealing with any configuration of the carbons normal to the "carbohydrate" group. On the other hand, we are confronted with a yield of furfural on hydrolysis such as has so far been exclusively established for certain of the carbohydrates, viz., the pentaglucoses, and for glycuronic acid (Tollens, *Agr. Vers. Stat.*, xxxix., 450). In further investigation of this problem, we have carried out a very large number of experiments upon the hydrolysis of the group, with subsequent oxidations by the well-known methods, in order to obtain the well-characterised dibasic acid derivatives of the $C_6$ or $C_5$ carbohydrates.*

Nitric acid oxidations have failed to yield definite products. We have studied this reaction exhaustively in all its stages. We find that the lignocelluloses (jute, wood, &c.) may be completely resolved by digestion at 70° C. with three times its weight of 10 per cent $HNO_3$. This decomposition of the fibre takes place with very slight action upon the furfural-yielding constituent. Distilled with hydrochloric acid in presence of urea the dissolved

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* From the *Ber. Deutsch. Chem. Gesell.*, November, 1893.

* The pronounced tendency of the hexoses to condense to furfural as a secondary result of oxidations, throws a great deal of light upon the oxidations of the carbohydrates, especially by nitric acid—more particularly the difficulty of obtaining satisfactory yields of the dibasic $C_6$ acids, excepting under carefully regulated conditions.

products yield from 30—40 per cent of their weight of the aldehyd. These soluble derivatives have been further treated by the well-known methods, viz.:—(1) Prolonged digestion with lime; (2) nitric acid of 1·15 sp. gr.; and (3) bromine and silver oxide: none of which have yielded any products of definite relationship to the "carbohydrate" group.

We would note here that Lindsey and Tollens (*Liebig's Annalen*, cclxvii., 341) were equally unsuccessful in dealing with a similar complex, viz., the soluble by-products of the bisulphite (Mitscherlich) process of preparing "cellulose" pulp from pine wood. To this complex they assign the formula $C_{24}H_{24}O_{10}.2(OCH_3)$, containing the unsaturated or hexene group, *i.e.*, representing the entire non-cellulose constituent of the wool. This is therefore to be compared with our jute lignone formula $C_{19}H_{22}O_9$, or $C_{17}H_{16}O_7.2(OCH_3)$. This product, obtained as a sulphonated derivative, was investigated by the methods which have been exhaustively studied and generalised by Tollens.

They obtained traces of levulinic acid, no saccharic acid, traces of mucic acid, and a small proportion of mannose and small quantities of pentaglucose, such as could be identified by the well-known colour reactions.

On the other hand, the main constituent was an amorphous gummy body, behaving as a homogeneous compound, and giving a series of synthetical products, all indicating derivation from a molecule with the empirical formula $C_{24}H_{24}O_{10}.2(OCH_3)$.

A tetrabromo derivative of this compound is easily formed, and we may assume that in the above formula one keto-R-hexene group is represented. Deducting for this group the approximate expression $C_6H_5O_3$, we are left with the residue $C_{18}H_{18}O_7.2(OCH_3)$. This residue, as explained, failed to give any "saturated" products of oxidation or hydrolysis; but, as in the case of the jute lignone, gives a large yield of furfural when distilled with hydrochloric acid.

In regard, therefore, to this important constituent of the non-cellulose of typical ligno-celluloses, we are for the present thrown back upon such further evidences as to constitution as are afforded by the empirical formulæ. Taking the C atoms in either formula, it will be found impossible to "saturate" them unless we assume that the whole of the O atoms are united to carbon only, and even then there proves to be an excess of carbon "affinities," to dispose of which a cyclic disposition must be assumed. We are not without some experimental verification of these conclusions.

On dissolving the "lignone" by the limited action of nitric acid (at 70° C.) as described. and subjecting the dissolved derivative to limited oxidation with chromic acid; on then adding acetate of sodium in excess, and boiling, furfural continuously distils. Even if therefore OH groups are fixed by the process of hydrolysis, the reverse condensation takes place under unusual conditions, implying an exceptional configuration of the C-nuclei.

The "lignone" group is further characterised by considerable avidity for acids generally, and "fixes" certain of these in an exceptional way, *e.g.*, chromic and nitric acid. It must also be remembered that the woods can be perfectly resolved by digestion with sulphurous acid (7 per cent aqueous solution) at 100° (Raoul Pictet), a reaction which could hardly be accounted for otherwise than by the basicity of the constituents dissolved, *i. e.*, the predominance of a $H_2C.O.CH_2$ configuration. We shall not pursue the discussion of these problematical groups into speculative directions. We have shown that all attempts to connect them with "carbohydrates" of known constitution have failed. We have indicated the lines of further investigation suggested by these negative results. We hope before long to communicate a more definite account of these peculiarly "condensed" products of vegetable growth.

In conclusion we revert to the consideration of the fibre substance as an integral compound, but admitting of resolution into the groups which we have now considered in detail. We have on several occasions criticised the view, which appears to be widely current, that the lignified tissues and films are mixtures of cellulose and the *non-cellulose* in "lignin" group of compounds. The relationships which we have shown to subsist between the constituent groups of the jute fibre are sufficient to disclose in them synthetical activity in various directions, and it can hardly be doubted, *à priori*, that these are exerted reciprocally between the groups.

It is also to be inferred from the relationships of the groups that the connection is a genetic one.

Thus the cellulose $\alpha$ has been shown to be susceptible of condensation to furfural, and this property has been definitely connected with oxidation of the normal celluloses, of which it is a secondary result.

Cellulose $\beta$ is further differentiated by the presence of the $O.CH_3$ group. In the non-cellulose or lignone complex we have a third group with these characteristics developed in such a way that furfural is obtained from it by the simplest of hydrolytic treatments; this group is, however, still "saturated" in the sense that it is free from $C = C$ groups, although, on the other hand, condensation to this form takes place with the greatest facility. In the last group we find the $C=C$ grouping associated with CO in a closed ring.

Regarded therefore in series, each group contains a prominent suggestion of the next-succeeding, and according to later developments of chemical theory it is not a very bold hypothesis that they constitute a genetic series. We make no assertion that the physiology of lignification is to be so explained, but the suggestion, we think, deserves serious consideration.

We wish to express our obligation to Mr. J. C. Chorley for valuable assistance in connection with this work.

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# NOTE ON THE INDICATORS USED IN TITRATING WITH STANDARD SULPHIDE SOLUTIONS.

By P. WILLIAMS.

The indicator commonly used is a solution of lead acetate with caustic soda. The solution is best made by adding to a solution of sodium tartrate a small quantity of caustic soda and lead acetate, then heating till the liquid is clear. Another substance which may also be used as an indicator is the compound sodium nitroprusside, which gives an intense violet colouration with a trace of sulphide, but it is inferior to the lead solution in delicacy, though in some circumstances it may be found more convenient than the lead. Sodium nitroprusside may be prepared by heating powdered potassium ferrocyanide with two parts of concentrated nitric acid diluted with an equal volume of water, until ferric chloride ceases to give a blue precipitate. The cooled solution is filtered off from the potassium nitrate, saturated with soda, and evaporated nearly to crystallisation; four parts of alcohol are then added and the compound filtered off. It is very soluble in water, but only a light coloured solution is needed in testing for sulphides. Drops of it are spread over a white tile, and the solution to be tested added in drops.

The delicacy of both these indicators was determined by gradually diluting with water a sulphide of known strength until the colour was visible when a drop was added to a drop of the indicator. 0·0000982 grm. of $Na_2S$ in 1 c.c. of water may be recognised by means of the sodium nitroprusside, and 0·0000245 grm. of $Na_2S$ in 1 c.c. by means of the lead test solution.

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ON THE

## TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Continued from p. 225.)

After this survey of the elements the question is naturally asked whether they form the sole constituents of the earth and of the cosmic system? In answering it Prof. Lothar Meyer again follows Bunsen's method, who was wont to point out that although the amount of the earth immediately accessible is small, it might be inferred from the composition of substances formed on it, as well as from that of the primæval crystalline rocks, that the same elements occur in the interior as are found on the crust; moreover, it might likewise be concluded from the analyses of numerous meteoric stones that the entire planetary system is composed of the same elements.

By means of spectrum analysis we have extended this inference to almost the whole visible universe. Whilst considering the chemical nature of the earth's surface, it is convenient to refer to the calculation of F. W. Clarke, according to whom 99 per cent of such parts of the earth as we can examine is made up of the nine elements O, Si, Al, Fe, Ca, Mg, Na, K, and H, and the remaining 1 per cent of all the other elements put together.

The student having now acquired a general idea of the nature of the distribution of the chemical elements, Dr. Meyer proceeds to discuss the rules according to which they enter into combination. The establishment and development of stoichiometry and of the atomic theory are described historically and briefly; likewise the electro-chemical theory, at least so much of it as is to-day applicable. The contrast between positive and negative is especially explained, and the influence of contact in chemical reactions experimentally shown. Opportunity is here taken to recall to the memory of the student the laws of the galvanic current so far as they find application later, and especially is Faraday's Law of Electrolysis elucidated in general terms.

The determination of electrolytic equivalents is then mentioned, together with the thermo-chemical equivalents deduced according to the Law of Dulong and Petit. The relations of both to chemical equivalents are exhibited by the aid of specific substances. Isomorphism is at the same time briefly spoken of, and reference is again made to the Law of Avogadro, already made mention of in connection with the synthesis of water.

During the Course all these doctrines are again spoken of on their later application; but a preliminary knowledge of them is needed at this stage, since the atomic weights and their relations to one another as the basis of the systematic arrangement are discussed, according to which both elements and compounds are to be described in the special part of the Course.

The student has now acquired some idea of atomic weights and the rules by which they are determined. The natural system of the elements is then explained from a chart on the wall of the lecture theatre. Professor Lothar Meyer supplements his description by the aid of one or other of the models which have been devised for the purpose.

After these preliminaries it might now appear the simplest to begin with the consideration of Family I.—the Alkali Metals. This Professor Meyer has tried, and, although possible, found inconvenient owing to the necessity of having to mention so many substances hitherto not spoken of. The usual way of starting with the non-metals offers so many advantages that no teacher would willingly abandon it. That, however, is not necessary, for the Course can be adhered to quite strictly, according to the periodic system, without breaking down old traditions.

As hydrogen has served for long as the unit of atomic weight on whose numerical value the natural system of the elements rests, it appears right to begin the consideration with the compounds of this element. How this can and must be done in a concise, comprehensive, and instructive way has been shown, as is known, by von Hofmann in his masterly "Introduction to Modern Chemistry." Following this method pretty generally, but with some alterations in details, Professor Lothar Meyer presents to his students the four chief types of hydrogen compounds—

$$HR : H_2R : H_3R : H_4R,$$

and, as is self-evident, he begins with the simplest type, with the hydrogen compounds of Family VII.—the Salt-formers. The place of these elements in the system is at first not specially emphasised; it is merely said that they all belong to one family, and at the same time the reason given for their being first mentioned is that their hydrogen compounds are the simplest of all. The experimental treatment of these hydrogen compounds is easily accomplished without the necessity of speaking of things hitherto unmentioned. A certain knowledge of the elements has been acquired in the introduction. Salt and its analogues are generally known or are readily learnt. The useful sulphuric acid is likewise known as oil of vitriol; its composition is simply given, and the usual proofs of it are referred to later on. Instead of beginning with hydrofluoric acid, Dr. Meyer prefers to take hydrochloric acid, which is prepared before the class, reduced, oxidised, synthesised, and electrolysed in the general way. Its volume relations are particularly noted and compared with those of water and of its constituents. From hydrochloric acid it is convenient to pass on to hydrofluoric acid, which is prepared by analogous methods, and then to hydrobromic and hydriodic acids.

Of the next type, $H_2R$, water has already been so thoroughly considered that it is now only mentioned. Hydrogen peroxide, which could be discussed in connection with it, is briefly referred to, and its fuller consideration is postponed until barium peroxide is treated. Hydrogen sulphide, the preparation of which has some analogies to that of hydrochloric acid, is now dealt with. The hydrides of selenium and tellurium are only mentioned; on the other hand, hydrogen persulphide is shown, as also how liquid hydrogen sulphide is obtained by means of it.

Of the third type all the known members, $NH_3$, $PH_3$, $AsH_3$, and $SbH_3$, are experimentally prepared. The compounds of the same elements poorer in hydrogen, $N_2H_4$, $N_3H$, $P_2H_4$, $P_4H_2$, are now described and their composition explained.

Of the fourth type, together with marsh gas and silicon hydride,—the only representatives of the type,—the higher hydrocarbons are briefly mentioned and shown, but their fuller consideration is referred to organic chemistry.

The hydrogen compounds of the metals are not spoken of here, but are deferred until the metals come up for consideration.

After the four types have been discussed the table of atomic weights is again referred to and the following survey given:—

$HF = 1 + 19{\cdot}06 = 20{\cdot}6$
$HCl = 1 + 35{\cdot}37 = 36{\cdot}37$
$HBr = 1 + 79{\cdot}76 = 80{\cdot}76$
$HI = 1 + 126{\cdot}54 = 127{\cdot}54$

$H_2O = 2 + 15{\cdot}96 = 17{\cdot}96$
$H_2S = 2 + 31{\cdot}98 = 33{\cdot}98$
$H_2Se = 2 + 78{\cdot}87 = 80{\cdot}87$
$H_2Te = 2 + 125 = 127$

$H_3N = 3 + 14{\cdot}01 = 17{\cdot}01$
$H_3P = 3 + 30{\cdot}96 = 33{\cdot}96$
$H_3As = 3 + 74{\cdot}9 = 77{\cdot}9$
$H_3Sb = 3 + 119{\cdot}6 = 122{\cdot}6$

$H_4C = 4 + 11{\cdot}97 = 15{\cdot}97$
$H_4Si = 4 + 28{\cdot}3 = 32{\cdot}3$

from which the dependence of chemical value, and accordingly also of chemical behaviour, on atomic weight is made evident. At the same time it is obvious that the generalisation follows, that quite analogous relations prevail throughout the natural system if we consider in compounds the monovalent salt-formers instead of the practically unknown hydrides.

This part of the Course, which has already been sketched out, is so arranged that it can be overtaken before the Christmas vacation. With the New Year the description of all the families according to the natural system and in the order of their atomic weights is systematically begun. It is, however, well to note that it is not generally advisable to treat the allied sub-groups along with the main groups, especially when they are connected with these by a few properties only, *e.g.*, the valency and isomorphism of their compounds. Their consideration is best left till later.

(To be continued).

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# THE ACTION OF IZAL ON THE PTOMAINES.

By A. B. GRIFFITHS, Ph.D., F.R.S. (Edin.), &c.

The new non-poisonous disinfectant known as "Izal" was extracted by Mr. J. H. Worrall, F.C.S., from an unknown oil obtained from certain coke ovens.

As Dr. W. B. Clarke has described in the columns of *The Lancet* (July 1, 1893) the treatment of wounds with "Izal," and as Dr. E. Klein, F.R.S., has investigated its action on pathogenic microbes, proving it to possess remarkable germicidal properties, I determined to test its action on the poisonous *ptomaines* which are produced in the system during the course of infectious diseases.

Until recently the vegetable kingdom was regarded as the only source from which alkaloids could be obtained, but it is now known that bodies which are very similar to the vegetable alkaloids are elaborated in the animal tissues, excretions, secretions, &c.,* and can be obtained therefrom by suitable methods of extraction.

The animal alkaloids, ptomaines, or toxines, are produced during the putrefaction of animal matter, and they are abundantly found in the animal tissues and fluids in pathological states. The urines of persons suffering from scarlet fever, diphtheria, pneumonia, erysipelas, puerperal fever, measles, parotitis, eczema, &c., have all yielded in greater or lesser quantities alkaloidal substances or ptomaines which are extremely poisonous in the isolated state. As a rule the ptomaines are the specific products or chemical principles elaborated in the body as the result of the existence of microbes.

At the outset it may be stated that I have extracted and described eleven ptomaines which occur in the urine during certain infectious diseases (see Griffiths's papers in the *Comptes Rendus*, tomes cxiii.—cxvi.); and among these ptomaines are those described in this paper.

The experiments recorded in this paper were undertaken in order to ascertain the action of "Izal" on the ptomaines which occur in the system during certain infectious diseases. It is essential in the treatment of infectious diseases that not only pathogenic microbes should be destroyed, but also the poisonous substances, or ptomaines, which they indirectly produce.

The "Izal" used in the experiments was diluted with distilled water in definite proportions, and the action of the various aqueous mixtures was tried directly upon the poisonous ptomaines.

*Scarlatinine* ($C_5H_{12}NO_4$) is the poisonous ptomaine of scarlet fever, and produces the disease when injected into the system of susceptible animals. To try the action of "Izal" on this ptomaine the following mixtures of "Izal" and water were prepared:—

1 part of "Izal" in 100 parts of water.
1 " " 200 " "
1 " " 500 " "
1 " " 1000 " "
1 " " 1500

3 c.c. of the aqueous mixtures were mixed with 0·5 grm. of scarlatinine in each case. In the first four cases, the poisonous properties of the ptomaine were destroyed; but when the "Izal" was diluted to the extent of 1 in 1500 it failed to destroy the poisonous properties of the ptomaine in question. In the experiments with the weaker mixtures (1 in 500 and 1 in 1000), the mixtures of the ptomaine, "Izal," and water had to be warmed before the toxic properties were completely destroyed. The products of the action of "Izal" on scarlatinine, being non-poisonous, may readily be taken into the system, or administered to animals with impunity.

*Puerperaline* ($C_{22}H_{19}NO_2$) is the ptomaine of puerperal fever. It is highly poisonous, and when administered to a dog it produced death within twelve hours. To try the action of "Izal" on puerperaline the following mixtures of "Izal" and water were prepared:—

1 part of "Izal" in 150 parts of water.
1 " " 300 " "
1 " " 500 " "
1 " " 1000 " "
1 " " 1500 " "

3 c.c. of the aqueous mixtures were mixed with 0·5 grm. of puerperaline in each case, and with the complete destruction of the poisonous ptomaine. It may be suggested that a mixture of 1 part of "Izal" in 1000 or 1500 parts of water would form a suitable lotion for preventing puerperal fever declaring itself.

*Diphtherine* ($C_{14}H_{17}N_2O_6$) is the poisonous ptomaine of diphtheria, and is produced in pure cultivations of *Bacillus diphtheriæ*. To try the action of "Izal" on diphtherine, the following mixtures of "Izal" and water were prepared:—

1 part of "Izal" in 500 parts of water.
1 " " 1000 " "
1 " " 1500 " "

3 c.c. of the aqueous mixtures were mixed with 0·5 grm. of diphtherine in each case; and each mixture rendered the ptomaine inert.

*Erysipeline* ($C_{11}H_{13}NO_3$) is the poisonous ptomaine of erysipelas. It produces high fever and death within eighteen hours. The strengths of the "Izal" mixtures used in the experiments were as follows:—

1 part of "Izal" in 750 parts of water.
1 " " 1500 " "
1 " " 2000 " "

3 c.c. of the aqueous mixtures were mixed with 0·5 grm. of erysipeline in each case, and each mixture rendered the ptomaine inert.

*Glycocyamidine* ($C_3H_5N_3O$) is the poisonous ptomaine of measles. The same mixtures of "Izal" as used in the experiments with erysipeline destroyed this ptomaine, or, in other words, the products formed by the action of "Izal" on the ptomaine were non-poisonous.

*Parotitis.*—The ptomaine ($C_6H_{13}N_3O_2$) of parotitis (Chemical News, vol. lxi., p. 87) is highly poisonous, and when administered to a cat it produced nervous excitement, cessation of the salivary flow, convulsions, and death. 3 c.c. of "Izal" (1 part in 2000 parts of water) readily destroyed 0·5 grm. of the ptomaine of parotitis.

*Pneumonia.*—The poisonous ptomaine ($C_{20}H_{26}N_2O_3$) of pneumonia was rendered inert by "Izal" (1 part in 1200 parts of water).

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* See Dr. A. B. Griffiths's "Manual of Bacteriology," pp. 303—324; and "Researches on Micro-Organisms," pp. 86—141.

*Glanders*.—The ptomaine ($C_{15}H_{10}N_2O_6$) of glanders is highly poisonous. A solution of it injected under the skin of a rabbit produced an abscess at the point of the injection, nodules in the lungs, spleen, and other organs, and, finally, death. This ptomaine was rendered inert by "Izal" (1 part in 800 parts of water).

In each of the above cases, the innoxious nature of the products formed by the action of "Izal" on the ptomaines was proved by experiments on animals; and such experiments were performed for me by a scientific *confrère* in France. After the action of "Izal" on each ptomaine, the characteristic tests failed to prove the presence of the smallest trace of ptomaine among the products.

From these experiments there is no doubt that "Izal" is a powerful agent, which readily destroys the deadly poisons produced in the system during the course of infectious diseases. Hence the reason that "Izal" should have a wide application in the treatment of infectious diseases, as it has the power of eliminating the poisonous ptomaines from the system.

In conclusion, I wish to record my obligations to Professors Brown-Séquard, Gautier, and Miquel, and to the late Dr. Charcot, of Paris, for the interest which they have taken in my own researches on the ptomaines; and I thank Messrs. Newton, Chambers, and Co. for the samples of "Izal" used in this investigation.

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## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 229).

### *The Absorption of the Most Refrangible Rays of Aluminium, Nos.* 30, 31, *and* 32.

A. *In Quartz*.—The observation was effected exclusively by means of photography. The absorption spectra were taken by means of the above-named spectroscopic apparatus, with a focal distance of 150 m.m. on highly sensitive plates (Zettnow). The source of light was a Leyden jar spark of the above-mentioned inductorium, 25 c.m. in length, striking between aluminium wires. Some photographs were also taken of the light of a tungsten spark, which is particularly suitable for absorption experiments on account of the uniformity of the distribution and the efficiency of its rays. The quartz plates the absorption of which was to be determined had been cut at right angles to the principal crystallographic axis, and their thickness was 3·0, 3·6, 5·2, 20, and 50 m.m. Their absorption was ascertained as follows:—

I covered the aperture of the collimator slit with the plate in question and then took (increasing constantly the time of exposure) a series of photographs of the aluminium spectrum placed below each other. I then removed the plate from the slit and repeated the series either with the same time of exposure or with one proportionately abridged. The difference between the two series showed then the absorption of the rays in question in the quartz plate selected. For demonstrating very small differences of such parallel photographs, and also where the inevitable small fluctuations of the luminosity of the source of light have to be taken into account, both spectra were photographed simultaneously. For this purpose I covered the slit for half its length with the quartz plate, whilst the other half of the slit was freely traversed by the rays. I thus obtained on each exposure two spectra separated from each other by a very narrow stripe of light, derived from the lateral surface of the quartz plate. The differences of these spectra are due as before to the absorption of light in the quartz plate.

It is found on comparison that in such proofs all distinctions come more sharply to view than in those where the photographs are successively brought into the field of vision. For thicker plates this process is less suitable, since the breadth of the stripe of light increases with the thickness of the plate and becomes ultimately wider than the object of the photographs admits. The loss of light which the rays undergo by reflection from the plane parallel surfaces of the quartz plate was so trifling in my proofs that it could be disregarded without injury to the trustworthiness of my result.

As will be self-evident all the proofs have only a very relative value. For as the prism and the lenses of the spectroscope employed consist likewise of quartz the proofs do not represent merely the absorption of the plate of quartz inserted in the track of the rays, but those of a much thicker plate. The mean total thickness of the prism and the lenses of the apparatus is 21 m.m. My proofs have therefore been produced with an uncovered slit under the influence of a stratum of quartz of the thickness of 21 m.m., and their parallel proofs consequently show merely how much more light is absorbed by the quartz plate covering the slit. As to the real resistance of the quartz no one of these proofs gives a decision. For this purpose there would be required prisms and lenses of a material absolutely impervious to the ultra-violet rays.

I give subsequently only the results of plates of 3, 20, and 50 m.m. in thickness. They show in what degree the mass of quartz retards the action of the most refrangible rays.

Quartz plate 3 m.m. in thickness. Aluminium sparks. Width of slit, 0·080 m.m. Exposure, 2½, 5, 10, 20 secs. One proof at each with and without the quartz plate Both series differ very little from each other, but the proofs with the plate are uniformly less intense than the others. This distinction is most distinct in the line No. 32, and as it is quite clear at all exposures it can be observed there better than in the other lines.

Quartz plate 20 m.m. in thickness. Aluminium sparks. Width of slit, 0·080 m.m. Exposure, 15, 30, 60, 90, 120, 180, 240, 300 seconds; a proof with the plate at each and a proof without the plate at 5, 10, 20, 40 seconds. In all the proofs the quartz plate has completely absorbed all the rays (Nos. 30, 31, 32), whilst without the quartz plate No. 32 appeared entirely, No. 30 only in 20 and 30 secs., and No. 31 with its less deflected component only in 30 seconds.

Quartz plate 50 m.m. in thickness. Aluminium sparks. Width of slit, 0·080 m.m. Exposure, 30, 60, 90, 120 secs.; one proof each with the plate, and 5, 10, 20, 40 seconds one proof each with the plate. No trace of the lines in question appeared, just as with the 20 m.m. plate.

All other proofs gave similar results.

Hence, in thick strata, quartz is to a great degree sparingly permeable for the most refrangible rays of the ultra-violet. My former proofs of the most refrangible ultra-violet had therefore been under the restraining influence of the prisms and lenses employed. Possibly their want of transparence was mainly to blame for the non-success of the proofs of the spectral region lying beyond 182 $\mu\mu$. As long as I continued working with quartz I could scarcely expect better results than heretofore. To obtain prisms and lenses more permeable for the ultra-violet had hence become an absolute necessity. If I was not willing to occupy myself with the search for suitable materials, I was then restricted to fluor-spar. In fact all the subsequent proofs, even those which will be at once discussed, the absorption spectra of gelatin, have been executed with prisms and lenses of white fluor-spar.

Faultless fluor-spar in colourless crystals ranks among rarities. The coloured varieties which are less difficult to obtain are not sufficiently transparent to come into

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

consideration for photographing the most refrangible rays. Moderately large specimens of the colourless material are never optically pure. Cracks, flaws, and other defects occur here and there, and interfere more or less with the optical effect of apparatus prepared from such materials, often, as I have myself repeatedly experienced, to such a degree as to render them useless where the production of clear images is required. It is not too much to say that to procure large faultless apparatus of white fluor-spar must now be classed among impossibilities. Quartz, or even calc-spar, may be found of faultless quality much more frequently than pure white fluor-spar. Under these conditions the procuring of fluor-spar for my spectroscopic apparatus would have been impracticable if Herr Carl Zeiss, of Jena, had not taken a profound interest in my work and assisted me in the most disinterested manner. Although he does not profess to supply fluor-spar apparatus, he has given me, besides a large prism (70°), the requisite lenses and closing-plates (plane parallel), all wrought of unusually pure fluor-spar, and with the refractive surfaces of the utmost perfection, for the extension of my observations on the ultra-violet. My permanent gratitude is due to Herr Zeiss for this active support, which has yielded in the sequel the most beautiful fruits.

(To be continued).

## RECENT ADVANCES IN AGRICULTURAL CHEMISTRY.

M. Georges Ville, whilst upholding the main principles laid down in his works and in his earlier lectures, has not been idle. He has continued observing and experimenting, and has in particular developed his doctrine of "sideration." It has been proved, by careful experiments both in France and in other countries, that certain plants are capable of absorbing the free nitrogen of the air and of retaining it in their tissues. Such plants are those especially of the leguminous order—peas, beans, tares, clover, &c. These plants, as practical agriculturists are fully aware, do not require ammoniacal salts, nitrates, or other nitrogenous manures; they obtain the nitrogen needed for their growth from the air. Now, by "sideration," M. Ville understands the cultivation of these plants as a material for fertilising the soil for the benefit of subsequent crops, *e. g.*, of wheat or other plants which do not derive their supply of nitrogen from the atmosphere to any sufficient extent. M. Ville, and those who accept his views, sow, *e.g.*, clover, and plough it into the soil, as he has fully explained in his writings, such as "The Perplexed Farmer," an English version of which, from the pen of Mr. W. Crookes, F.R.S., has been published (Messrs. Longmans). The field of clover, &c., is thus made to play more conveniently and economically the part assigned by the old school of agriculture to cattle kept for the mere production of manure—"straw-treaders" as they are technically called.

With the exaggeration customary in controversy M. Ville has been accused of pronouncing cattle-keeping an error. This is by no means correct. Where there is at hand a good market for milk, butter, cheese, meat, or for wool, he upholds live stock as remunerative. But how, he asks, can any number of cattle at once supply manure to keep their pasture-land fertile, and at the same time supply manure for the arable land? The more his teachings are adopted the more shall we be delivered from the disgrace and the barbarism of "permanent pasture."

The keeping of stock for the manufacture of manure is one of the unhappy agencies which are depopulating the country and driving the peasantry to fester in the slums of our great cities under conditions no less demoralising than anti-sanitary.

It has been said that the man who makes two ears of corn grow where formerly there grew only one is a benefactor to his species. The great naturalist Buffon said, in a very similar manner, "Where a loaf is created a man springs up," but he forgot to add, Woe to the nation where men arise without the loaves! Now M. Ville has shown practically how the supply of food may be vastly increased. For this he merits the highest honours. Painful it is to be compelled to add that he evidently does not meet with the recognition to which he is so fully entitled. Perhaps in a couple of centuries a statue to his memory will be erected amidst official acclamations! His view as to the benefit which France may derive from agricultural improvements is, however, over-strained. All the advances in farming which are possible in France are no less possible in Spain, in Hungary, South Russia, Canada, or Australia. Hence France can never dictate the price of wheat or other necessaries of life; she must always be under-sold by countries where land is more abundant, the climate better, and local burdens less heavy.

## ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.*

By THEODORE WILLIAM RICHARDS and ELLIOT FOLGER ROGERS.

In the course of an investigation upon the atomic weight of copper, recently conducted in this Laboratory, it was noted that cupric oxide prepared by the ignition of the nitrate always contains a considerable amount of occluded gas, which is composed mainly of nitrogen.† Cupric oxide prepared from the carbonate, on the other hand, appears to possess no such property of occluding gases. Since the material used by Hampe and others had all been made by the former method, it was at once evident that the occluded gas contained in the oxide was wholly responsible for the formerly accepted erroneous results for the atomic weight of copper.

The results of these experiments suggested the possibility that gases might be occluded by all oxides prepared in this way from the nitrates. It became a matter of much importance to test the point, for such oxides have often furnished the starting-point for determinations of atomic weights.

The method adopted in the present research was precisely similar to that used in the case of the cupric oxide. Since it is by no means certain that indefinite heating in a vacuum could drive out all the gas from the compact, often crystalline compound under examination, the material was dissolved in acids under such conditions that the gas set free could be measured and analysed.

The simple apparatus needed has been described and explained in the paper already quoted. The material to be investigated was placed in the largest bulb of the bulb-tube shown in the accompanying diagram, and the

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* Contributions from the Chemical Laboratory of Harvard College.

† Theodore W. Richards, *Proceedings of the American Academy of Arts and Sciences*, xxvi., 281. In 1868 Frankland and Armstrong pointed out this fact; but their statement lacked definiteness, and has since been largely forgotten.

tube was about half-filled with cold water which had been thoroughly boiled. The whole was then connected with the water-pump, and freed from adhering air-bubbles by agitation in the partial vacuum, the water being allowed to boil gently under the reduced pressure. Subsequently the tube was filled with boiled water, and returned to its normal horizontal position. Pure acid was now run in from a pipette, a short piece of glass rod within the large bulb furnishing a means of agitating the oxide during its solution. The gas which was set free was finally collected and measured in the sealed end of the apparatus. In the concluding experiments, where greater accuracy was desired, the gas was transferred, and re-measured in a tube which had been carefully calibrated by means of mercury.

The gas was analysed with the help of a small Hempel's apparatus made for the purpose. The burette with which the first ten analyses were made was about 7 m.m. in internal diameter, and could be read to a 50th of a c.c., while that used for the later analyses was only 4 m.m. in diameter, and could be read with reasonable certainty to the 100th. The portion of the gas absorbed by caustic potash was assumed to be carbon dioxide, and the furrher portion which was absorbed by alkaline pyrogallol was assumed in like manner to be oxygen. The residue was perfectly inert, and was undoubtedly nitrogen. One sample of this residue obtained from zincic oxide was mixed with oxygen and subjected to the spark of an induction coil, without diminution in volume. The apparatus and chemicals were tested from time to time by analyses of air.

In every case the gas, while saturated with aqueous vapour, was measured at the ordinary temperature and atmospheric pressure of the room. The variations from the mean values of 22° and 76·0 c.m. were not sufficient to need attention in crude work of this kind, when working upon such very small quantities of gas.

### *Zincic Oxide.*

Preliminary experiments with this substance gave results exactly corresponding to those obtained from cupric oxide. If the substance was prepared by ignition of the nitrate, very considerable amounts of gas were found to be occluded; while material of a similar grade of purity in every other respect, made by heating zincic carbonate, appeared to contain no trace of gas.

The oxide used in the first three experiments was made by treating so-called pure zinc with nitric acid, evaporating to dryness, re-dissolving the zincic nitrate in water with the addition of a little nitric acid, precipitating a small amount of iron with ammonia in slight excess, evaporating the filtrate, and igniting the residue. This gave a faintly yellow oxide.

For the second series a nearly neutral solution of fairly pure zincic chloride was precipitated while boiling by a solution of sodic carbonate. Part of the basic carbonate thus formed was ignited directly, the oxide thus produced containing no occluded gas (Experiment 4). The remainder was dissolved in nitric acid, evaporated to dryness, and ignited to the full heat of the blast lamp in an open porcelain crucible. Experiments 5, 6, and 7 are analyses of this yellowish sample.

For the third series a solution of "chemically pure" zincic nitrate was allowed to stand over an excess of zinc for some time. The filtered solution was evaporated until a portion of the nitrate had been converted into the basic salt. The whole was then poured into distilled water, and a solution of normal nitrate was thus obtained after the basic salt had been filtered off. This solution was treated a number of times with zincic hydrate—which had been precipitated by ammonia and washed until free from the salts of this base—and allowed to stand. The filtered solution was evaporated to dryness, and heated in a porcelain crucible to about 240° C. over a ring burner. Part of this was analysed at once (Experiment 8), part heated by a Bunsen burner (Experiments 9 and 10), and part ignited at a very high temperature in a Hempel clay furnace with the blast-lamp and bellows (Experiments 11 and 12). Experiment 13 was made with a soft white oxide prepared from the basic nitrate.

Analyses 14 to 27 inclusive were made from oxide obtained as follows. Pure white zincic oxide of commerce was dissolved in nitric acid, and carefully washed zincic carbonate was added to this solution in slight excess. The whole was allowed to stand with occasional shaking for some time, and finally filtered and evaporated rapidly by boiling. This gave a sample of the oxide, which was very nearly white after intense heating in a double porcelain crucible.

In Experiments 22 and 23, pure oxygen was introduced into the flame of the blast lamp used for igniting the zincic oxide, the bottom of the outer crucible being melted where the flame struck it. The material analysed in Experiment 22 was taken from the layer nearest to the zincic silicate formed in the bottom of the crucible by fusion of the glaze, and that used in Experiment 23 was taken from the top. The zincic oxide of Experiment 24 was heated to bright yellow heat in the same way. All the edges of the porcelain were rounded, and the cover and the crucible itself were fused to the heavy iron supports on which they rested. After twelve minutes the iron itself began to burn and the ignition was stopped. The oxide was found to be "sintered together," and was of a greyish colour, as if it had been reduced in part. The inference was corroborated by the presence of zincic oxide on the cover of the crucible and on the sides of the stack of the furnace. The zincic oxide used in Experiment 25 was treated in a similar manner, but proved to be still darker in colour. It was afterwards ignited for some time in an atmosphere of oxygen in order that no reduced metal might be left.

The materials used in Experiments 26 and 27 were separate samples heated in a double crucible, with the cover of the inner crucible fitting inside the outer one, instead of covering both. This arrangement rendered less likely the entrance of reducing gases, and allowed freer play of air in the furnace. After the latter had been thoroughly heated by the ordinary blast lamp, oxygen was slowly turned on through a Y-tube to replace a large part of the air in the flame. This gave an intense white heat, which melted and burned the tip of a file in the fraction of a minute. In Experiment 27 the glaze of the inner crucible was fused, and the platinum which separated the two crucibles was cemented to the outer crucible. The crystalline residue of zincic oxide after this treatment was white, with the faintest trace of yellow, but no sign of grey. As the crucible would not stand a higher heat, and as any quantitative determination could scarcely be carried on at a higher temperature, no attempt was made to push the heat further.

The fifth series of determinations was made with the object of discovering whether the trace of silica and alkali dissolved from the glass and porcelain might be responsible for the occlusion of the gases. First, a sample of the purest zinc that could be obtained was treated with a small amount of pure nitric acid in a porcelain dish, and the solution evaporated to small bulk in the presence of an excess of zinc. Upon dilution the basic nitrate, which contained most of the impurities not deposited upon the zinc, was precipitated and removed by filtration. The solution was then evaporated to dryness, and the residue ignited in porcelain. (See Experiments 28 and 29). Another sample of zinc was dissolved in a similar way in platinum, and the resulting solution of the pure nitrate was divided into several portions. One portion was evaporated in glass and ignited in porcelain, the residue containing somewhat more gas than that which had been treated wholly in porcelain. (See Experiments 30, 31, 32, and 33). Another part was evaporated and ignited in platinum (Experiment 34). This sample was undoubtedly reduced in part by the diffusion of gases from the flame

| No. of Expt. | Wt. of Zincic oxide. | Time and Temp. of heating. | Vol. of Gas evolved. | Vol. of Gas calc. for 10 gr. of ZnO. | Analysis of Gas by volume. |
|---|---|---|---|---|---|
| | Grms. | | C.c. | C.c. | |
| 1. | 1·375 | Blast lamp. | 1·6 | 12·0 | |
| 2. | 1·19 | ,, | 1·45 | 12·2 | |
| 3. | 1·225 | ,, | 1·53 | 12·5 | |
| 4. | 1·1 | ,, | 0·00 | 00·0 | |
| 5. | 1·05 | ,, | 2·1 | 20· | $CO_2$= 1·2%<br>$O_2$=55·5<br>$N_2$=42·5 |
| 6. | 1·08 | ,, | 2·1 | 19·4 | |
| 7. | 1·075 | ,, | 2·15 | 20· | |
| 8. | 1·27 | 240° C. | 0·00 | 00·0 | |
| 9. | 1·005 | Bunsen flame. | 0·70 | 7·0 | |
| 10. | 1·065 | ,, | 0·78 | 7·3 | |
| 11. | 1·22 | Blast lamp. Hempel furnace. | 0·58 | 4·7 | |
| 12. | 1·91 | ,, | 0·92 | 4·8 | |
| 13. | 1·05 | Water blast. Hempel furnace. | 0·20 | 1·9 | |
| 14. | 1·07 | Water blast furnace 30 mins. | 0·75 | 7·0 | |
| 15. | 1·00 | ,, | 0·71 | 7·1 | |
| 16. | 1·02 | Blast. | 1·52 | 14·9 | $CO_2$= 1·3%<br>$O_2$=53·8<br>$N_2$=44·8 |
| 17. | 1·10 | Water blast furnace 2 hrs. | 0·35 | 3·2 | $O_2$= 9·1<br>$N_2$=90·9 |
| 18. | 1·20 | ,, 3½ ,, | 1·12 | 9·1 | |
| 19. | 1·06 | ,, 5 ,, | 0·83 | 7·8 | |
| 20. | 0·85 | ,, 6 ,, | 0·46 | 5·4 | |
| 21. | 0·92 | ,, 6½ ,, | 0·53 | 5·8 | |
| 22. | 1·07 | Furnace 6½ hrs. Oxygen flame, 15 mins. | 0·42 | 3·9 | $CO_2$= 0·0%<br>$O_2$=16·9<br>$N_2$=83·1 |
| 23. | 1·125 | The same. | 0·48 | 4·3 | |
| 24. | 1·03 | Oxy. fl. 15 mins. | 0·24 | 2·3 | $O_2$=16·7%<br>$N_2$=83·3 |
| 25. | 1·105 | 30 ,, | 0·19 | 1·7 | |
| 26. | 0·72 | White heat 20 mins. | 0·33 | 4·6 | $CO_2$=0<br>$O_2$=24%<br>$N_2$=76 |
| 27. | 1·0125 | White heat 35 mins. | 0·45 | 4·4 | |
| 28. | 1·05 | Water blast ½ hr. | 0·42 | 4·0 | |
| 29. | 1·019 | 1½ ,, | 0·37 | 3·6 | |
| 30. | 1·34 | Bunsen flame 30 mins. | 0·28 | 2·10 | |
| 31. | 1·05 | Water blast ½ hr. | 0·97 | 9·2 | |
| 32. | 1·0035 | ,, 1 ,, | 0·68 | 6·8 | |
| 33. | 0·9765 | ,, 1½ ,, | 0·63 | 6·4 | |
| 34. | 1·03 | ,, ½ ,, | 0·175 | 1·7 | |
| 35. | 1·08 | ,, ½ ,, | 0·35 | 3·2 | |
| 36. | 1·50 | ,, 20 m. | 0·82 | 5·46 | |
| 37. | 1·004 | ,, 1½ hr. | 0·68 | 6·8 | |
| 38. | 1·018 | ,, 2 ,, | 0·68 | 6·7 | |
| 39. | 1·00 | | 0·00 | 0·00 | |

*Remarks.*

*No.* 4.—From carbonate.
*No.* 8.—Gave test for nitrates.
*No.* 13.—Made from basic nitrate.
*No.* 14.—Fourth series.
*No.* 17.—Partly reduced.
*Nos.* 18—21.—Heated in double crucible by water blast in furnace. Samples removed from time to time.
*No.* 22.—Layer next the silicate.
*No.* 23.—Upper layer.
*No.* 24.—Partially reduced and re-oxidised.
*No.* 25.—Reduced more than Ex. 24 and re-oxidised.
*Nos.* 26 *and* 27.—White after ignition.
*No.* 28.—Fifth series.
*No.* 30.—Probably contained nitric acid.
*No.* 34.—Partially reduced.
*No.* 35.—Less reduced.
*No.* 36.—Possibly reduced in part.
*No.* 39.—Prepared from carbonate.

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(Erdmann, *Pogg. Annal.*, lxii., 611 ; Morse and Burton *Am. Chem. Journ.*, x , 311—321). Still another portion was ignited for a short time only in platinum, the ignition being completed in porcelain (Experiment 35). A fourth portion was ignited for a short time in an open platinum dish with free access of air (Experiment 36). Finally, the remainder of the solution of pure zincic nitrate was evaporated and ignited in a platinum vessel enclosed within one of porcelain. This specimen was not exposed to the action of reducing gases, and upon solution it evolved almost exactly the same amount of gas as the specimen which had been prepared in glass and ignited in porcelain. (See Experiments 37 and 38).

Experiment 39, using zincic oxide prepared from the carbonate, was made to test again the accuracy of the method.

The weight of zincic oxide taken for each individual experiment is tabulated in the second column of the accompanying Table, and the third column indicates approximately the conditions used for the ignition of the different portions. The volume of gas given off on the subsequent solution of the zincic oxide in sulphuric acid is recorded in the fourth column, while the fifth contains the same data reduced to the standard of ten grms. of zincic oxide. The sixth column contains a record of the analyses of the gases, and the seventh supplies information upon a few minor points connected with individual results.

It is evident that we are dealing here with a phenomenon similar both qualitatively and quantitatively to that observed in the case of copper. Zincic oxide prepared from the nitrate occludes a very appreciable quantity of nitrogen and a somewhat variable quantity of oxygen. Continued application of heat tends to drive out both gases, the oxygen being less firmly held than the nitrogen; but the highest heat which we were able to obtain was insufficient wholly to eliminate either gas. Under like conditions, specimens of zincic oxide made from zincic nitrate which had been obtained in a number of different ways appeared to hold approximately the same amounts of gas. It is almost, if not quite, impossible to prepare the oxide in this manner in a state wholly free from solid impurities taken from the containing vessel during the ignition of the purest possible zincic nitrate. The effort was made in the preceding series of analyses to prepare samples which must contain wholly different kinds of impurities. The fact that these different samples contained almost equal amounts of gas shows with reasonable certainty that the impurities are not responsible for the occlusion.

It is noticeable that the oxide obtained at a very low temperature, which still contained traces of zincic nitrate, contained little or no occluded gas (Experiments 8 and 30); also that six specimens which had been suspected of partial reduction contained much less gas than similar material free from this suspicion (Experiments 17, 24, 25, 34, 35, and 36).

(To be continued.)

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The Use of Hydrometers. — Fr. Maly (*Zeit. f. Instrumenten Kunde*) — The author shows that accuracy in the use of these instruments depends on the state of the spindles. He cleanses first from coarse impurities, and then rubs with a damp (but not *wet*) cloth. Friction with a dry cloth is useless. The cleansed instrument is then allowed to lie for a time, so as to permit of the evaporation of any adhering moisture.

# THE ELECTROLYTIC SEPARATION OF THE METALS OF THE SECOND GROUP.*

By SAMUEL C. SCHMUCKER.

Of recent years the determination of metals quantitatively by the methods of electro-chemical analysis has grown into great popularity. The exceedingly accurate results, the simple forms obtained, and the ease with which it is possible to determine the absolute purity of the deposits, all combine to make electrolytic methods highly desirable. Hitherto most of the operations have served simply to determine quantitatively the amount of one ingredient present, while comparatively less success has attended the separation of metals from each other. It is true that many valuable separations are known, the results of which have been published in the various chemical journals and in the few books devoted to the subject. But the list of separations of metals in the same group, and of separations of the different groups, is far from complete; and it is to this point that those chemists interested in electrolytic work are now giving their most earnest attention. Here the field seems at present likely best to repay the investigator.

As an example of a gap desirable to fill, I would cite the case of those metals known to analytical chemists as the *metals of the second group*, viz., arsenic, antimony, tin, mercury (ic), lead, bismuth, copper, and cadmium. We have no electrolytic method serving for the separation of the first three from any of the later members. An examination of the literature of the subject would disclose to the student of electrolysis that should he encounter, for instance, a mixture containing copper, arsenic, antimony, and tin, he would find himself advised to abandon the current and employ the usual gravimetric method of digestion with sodium sulphide to effect the separation of copper from the other constituents. Nor is this by any means a solitary example. It is true, individual separations have been made in this group. For example, Smith and Frankel (*Am. Chem. Journ.*, 12, 428) succeeded in separating copper from arsenic, both in cyanide solution and in ammoniacal solution in which the arsenic was in the form of pentoxide and there was much free ammonia. The results in this latter instance have been confirmed by McKay. Very recently, Smith and Wallace (*Journ. Anal. Appl. Chem.* vii., 4) have printed an account of their successful separation, in very varying proportions, of copper from antimony, in alkaline tartrate solutions. These are the first successful results where antimony was present as more than a bare trace. Copper has never been separated from tin. Cadmium has no recorded separation from either antimony or tin; it has, however, been separated by Smith and Frankel from arsenic in cyanide solution. The case is in no wise better with either lead or bismuth. Solutions of either of these with any of the other three (As, Sb, Sn) have defied separation. Concerning mercury (ic) there is little more to be said. If a mercuric solution contains also arsenic in the pentoxide form, and a decided excess of potassium cyanide, the mercury can be separated without difficulty. These results have suggested the question whether it is possible to find a general method suitable for the separation of any of the basic oxides of this second group from any or all of the acid oxides of the same group. This problem I have endeavoured to solve. The method employed by Smith and Wallace for the separation of copper from antimony, suggested that in the alkaline tartrates might lie the key to the situation; and the separations from arsenic suggested, also, that it would be well to have the acid oxides in their highest state of oxidation. The results have fully justified my utmost expectation, and so far as they have been prosecuted, have been uniformly accurate. Inasmuch as we already have a separation of copper from arsenic, and of copper from antimony, my first attention was turned to the separation of—

### *Copper from Tin.*

A solution of copper sulphate was made containing 0·0999 grm. of metallic copper in each portion measuring 10 c.c. About one-tenth of a grm. (varying from 0·1020—0·1057 grm.) of metallic tin was dissolved in hydrochloric acid, and bromine water added until the solution remained coloured with the bromine to insure complete oxidation. I was led to suspect the presence of iron in the tin, and as this metal is deposited by the current from an alkaline tartrate solution, it became necessary to secure its removal. The tin solution was accordingly evaporated to dryness, taken up with caustic soda, the solution diluted, the iron filtered off, and the filtrate containing the tin (as sodium stannate) was neutralised with tartaric acid. To this solution 4 grms. of tartaric acid were added and, as soon as this was thoroughly dissolved, 10 c.c. of ammonium hydroxide (sp. gr. 0·932). To this (after filtering off slight impurities brought in with the tartaric acid) 10 c.c. of the above-mentioned cupric solution (containing 0·0999 grm. copper) were added, the whole transferred to a platinum dish having a capacity of about 200 c.c., and the solution diluted to 175 c.c. with distilled water. A current, generated by five or six gravity cells, coupled in series, was run through the solution, the anode being a flat platinum spiral. There was a voltameter also in the circuit. The precipitation was started at 4 p.m., and allowed to run during the night. The currents employed most successfully generated from 0·4 c.c. to 1·2 c.c. of electrolytic gas per minute. Immediately on interrupting the current, the liquid contents of the dish (which should smell quite strongly of ammonia) must be rapidly poured off, luke-warm distilled water poured into the dish, allow to flow around the inside and gently emptied out. The washing with warm water should be repeated three or four times quite rapidly, and be followed by similar washings with small quantities of absolute alcohol. The dish can then be carefully dried on the edge of a warm plate, allowed to cool, and weighed. Great care must be exercised during the drying to see that the dish does not get too warm, or the metal will readily oxidise, for the copper deposited from an alkaline tartrate solution does not have the lustrous sheen of that precipitated from solutions containing free acid or potassium cyanide; it has a velvety dark red appearance, but is thoroughly adherent to the dish. If the current is strong enough to generate 1 c.c. of electrolytic gas per minute, the precipitation is complete in five minutes. A decided excess of ammonia has no deleterious effect. The following examples will serve to illustrate the operation:—

*Experiment* 1.—0·1087 grm. of metallic tin was dissolved in hydrochloric acid, oxidised, evaporated to dryness, taken up with water and sodium hydroxide, filtered, neutralised with tartaric acid, 4 grms. of solid tartaric acid and then 10 c.c. of ammonium hydroxide added. 10 c.c. of the copper solution (0·0999 grm. copper) were added, the whole transferred to a platinum dish, diluted to 175 c.c., and the current applied. The current delivered 0·4 c.c. of electrolytic gas per minute, and was allowed to act for seventeen hours. The deposit of copper weighed 0·1001 grm.

*Experiment* 2.—0·1039 grm. was treated as above. 10 c.c. of copper solution were used, 4 grms. tartaric acid and 15 c.c. of ammonium hydroxide added, and a current generating 1 c.c. of electrolytic gas per minute acted for fifteen and one-half hours. The precipitated copper weighed 0·0997 grm.

*Experiment* 3.—0·1044 grm. of tin was treated as before. 4 grms. of tartaric acid and 20 c.c. of ammonium hydroxide added, together with 10 c.c. of the copper solution. A current generating 1·2 c.c. electrolytic gas per minute acted for five hours. The deposited metal weighed 0·0997 grm.

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* From the *Journal of the American Chemical Society*, vol. xv., No. 4, 1893.

It having now been found possible to separate copper from arsenic, from antimony, and from tin, my attention was next turned to the possibility of separating copper from the other three collectively.

### *Copper from Arsenic, Antimony, and Tin.*

Here, guided by the experience of Smith, Frankel, and Wallace, I decided to have the three acid oxides in their highest state of oxidation. Accordingly the solutions were made up as follows:—A quantity of arsenious oxide weighing 3·3342 grms. was dissolved in nitric acid (sp. gr. 1·3), and the solution evaporated to dryness. The arsenic acid thus formed was taken up with water, any slight impurities filtered off, and the filtrate diluted to 250 c.c. with distilled water. This gave a solution containing 0·1009 grm. metallic arsenic in each 10 c.c. For the antimonic solution a portion of potassio-antimonious tartrate, $C_4H_4(SbO)KO_6+\frac{1}{2}H_2O$, was dissolved in water, diluted largely, and then boiled with addition of bromine water until the solution remained discoloured for a considerable time by the bromine, thus indicating the complete oxidation of the antimony. The addition of a small quantity of tartaric acid prevented the slight tendency to precipitation of oxysalts. The solution was filtered and diluted to 250 c.c., thus giving 0·1024 grm. metallic antimony in each 10 c.c. The tin solution was prepared as described under the section on copper and tin, and was made of such a strength as to contain 0·1031 grm. metallic tin to every 10 c.c. The copper solution was made by dissolving a little more than 20 grms. of copper sulphate and diluting to 500 c.c. Ten c.c. of this solution, as determined by direct trial, contained 0·1016 grm. metallic copper.

The solution which proved best for the separation contained 8 grms. of tartaric acid, 31 c. c. of ammonium hydroxide, and 10 c.c. of each of the solutions of copper, antimony, arsenic, and tin described above. Five hours proved sufficient time, and a current generating 0·8 c.c. electrolytic gas per minute proved of sufficient strength to effect a thorough precipitation of the copper entirely free from any of the other three metals. The copper has the same appearance as when separated from tin, and must be washed and dried in the same way. It is, however, absolutely necessary to keep the quantity of tartaric acid and of free ammonia as high as indicated, or antimony to the amount of fully one-half of that present will be precipitated. I give the following results:—

*Experiment* 1.—Eight grms. of tartaric acid were dissolved in water, 30 c.c. of ammonium hydroxide added, and the solution filtered. To this were added 10 c.c. of each of the solutions of arsenic, antimony, tin, and copper (0·1016 in 10 c.c.) previously mentioned, and the solution diluted to 175 c.c. The current generated 0·8 c.c. electrolytic gas per minute, and was allowed to act for five hours. The precipitated copper weighed 0·1019 grm.

*Experiment* 2.—Exactly the same quantities as in 1 were exposed with the same strength of current and for the same length of time. This resulted in the deposition of 0·1010 grm. of metallic copper instead of 0·1016 grm.

Having thus succeeded in the separation of copper, I next directed my attention to cadmium, and as antimony seemed to give the most trouble, I began with the separation of—

### *Cadmium from Antimony.*

The antimony solution was the one previously described. The cadmium solution was the nitrate, and contained 0·0916 grm. of the metal in 10 c.c. of solution as determined by electrolytic deposition from the cyanide solution. There is only one difficulty presented in this separation, and that is that the current must be weak, or the deposited cadmium will be too spongy to wash. Accordingly, it is necessary to allow the current to act through the night. The deposit of metal shows a tendency to form spongy masses here and there. These can be washed without loss if care be exercised in pouring the wash water on and off. The dish containing the deposit is washed with water simply—the washing with alcohol being unnecessary—and then dried on the edge of the hot plate. As actual results I give the following:—

*Experiment* 1.—Five grms. of tartaric acid were dissolved in hot water, 15 c.c. ammonium hydroxide were added, and the solution filtered free from impurities introduced by the acid. Ten c.c. of the antimony solution and 10 c.c. of the cadmium solution (0·0916 grm. metallic cadmium) mentioned above were added, the whole transferred to a platinum dish, diluted to 175 c.c., and the current allowed to act over night. The cadmium was washed with hot water and dried. It weighed 0·0920 grm.

*Experiment* 2.—The solution here was made up in the same way as in the preceding experiment. The current gave 0·3 c.c. electrolytic gas per minute. It acted over night. The cadmium deposit weighed 0·0925 grm.

*Experiment* 3.—The solution was just the same as in the last case. The current gave 0·4 c.c. electrolytic gas per minute, and acted for sixteen hours. The deposit of metallic cadmium weighed 0·0925 grm.

### *Cadmium from Tin.*

In this case the tin solution was the same as that employed in the separation of arsenic, antimony, and tin from copper; and, indeed, throughout the rest of these trials the arsenic solutions (0·1009 grm. metallic arsenic in 10 c.c), the tin solutions (0·1031 grm. metallic tin in 10 c.c.), and the antimony solutions (0·1024 grm. of antimony in 10 c.c.) are the same. The separation presents no difficulties, and the metal is deposited in good form if the precaution previously mentioned is observed, namely, to use a long-continued weak current. The metal should be washed with hot water only, and dried on the edge of a warm plate.

*Experiment* 1.—Five grms. of tartaric acid were dissolved in water, 15 c.c. of ammonium hydroxide added, then 10 c.c. of the tin solution, and 10 c.c. of the cadmium solution (0·0916 grm.). This was diluted to 175 c.c. in the platinum dish, and a current liberating 0·1 c.c. of electrolytic gas per minute allowed to act upon the mixture for eighteen and one-half hours. The cadmium deposit was washed with hot water, dried, and weighed. It equalled 0·0914 grm.

*Experiment* 2.—The conditions and quantities were here just the same as in the last experiment, save that the current delivered 0·2 c.c. of electrolytic gas and was allowed to act for eighteen hours. The cadmium weighed 0·0918 grm.

### *Cadmium from Arsenic.*

The solutions employed in this case were those used previously. The amount of tartaric acid was 5 grms., and of ammonium hydroxide 15 c.c. This quantity proved the best for all separations where but two metals were present, and was adhered to under these circumstances throughout the rest of the work. When more than two elements are present it becomes necessary to increase the amounts of tartaric acid and of ammonium hydroxide to 8 grms. and 30 c.c. respectively. The tartaric acid was dissolved in water as before, the ammonium hydroxide added, followed by the arsenic and cadmium, the solution transferred to the platinum dish, diluted to 175 c.c., and then electrolysed. The deposit differed in no wise from that obtained in the separation of cadmium from tin.

*Experiment* 1.—Five grms. of tartaric acid were dissolved in water, 15 c.c. of ammonium hydroxide were added, followed by 10 c.c. of the cadmium solution (=0·0916 grm. cadmium), and 10 c.c. of the arsenic solution. The mixture was introduced into a platinum dish, diluted to 175 c.c., and a current that gave 0·3 c.c. electrolytic gas per minute allowed to act for a period of sixteen hours. The cadmium deposit weighed 0·0913 grm.

*Experiment* 2.—Like quantities were taken and treated in the same manner, except that the current delivered 0·2 c.c. of electrolytic gas per minute. It acted sixteen hours. The cadmium deposit weighed 0·0921 grm.

### *Cadmium from Arsenic, Antimony, and Tin.*

The solution was now made up by combining the arsenic, antimony, and tin with the cadmium. The tartaric acid was increased to 8 grms. and the ammonium hydroxide to 30 c.c. The cadmium separated from the three differed in no respect from that separated from any one. It had the same appearance, and washed and dried in the same way.

*Experiment* 1.—Eight grms. of tartaric acid were dissolved in water, 30 c.c. of ammonium hydroxide were added, followed by 10 c.c. each of arsenic, antimony, tin, and cadmium solutions. The current liberated 0·25 c.c. of electrolytic gas per minute and acted for eighteen hours. The metallic cadmium weighed 0·0915 grm.

*Experiment* 2.—The same quantities were used as in Experiment 1. The current gave 0·4 c.c. of electrolytic gas per minute, and acted sixteen hours. The deposit of cadmium weighed 0·0920 grm.

*Experiment* 3.—Same quantities were used. The current gave 0·3 c.c. of electrolytic gas per minute, and precipitated 0·0918 grm. cadmium.

Copper and cadmium having yielded thus easily to the current in the presence of arsenic, antimony, and tin in ammonium tartrate solutions, my attention was next turned to bismuth.

(To be continued).

## NOTICES OF BOOKS.

*On Sewage Treatment and Disposal.* For Cities, Towns, Villages, Private Dwellings, and Public Institutions. By Thomas Wardle, F.C.S., F.G.S. Manchester: Heywood. Large 8vo, pp. 408.

The author of this volume has passed from the chemistry of colours and their application to that of sewage and its impurities. We are glad to find that he does not accept irrigation as the universal method of dealing with the sewage difficulty, but depends more upon chemical processes. Of these he describes many as carried out in different localities. He quotes the standards of the late Rivers' Pollution Commissioners, or rather of Professor E. Frankland, F.R.S., since his colleagues in that memorable and costly inquiry, being neither chemists nor physicians, must have accepted his guidance. Mr. Wardle expounds the part played by bacteria in the putrefaction of sewage and of imperfect effluents. This is a novel feature in works on the disposal of sewage. The Dibdin process, inherited by the London County Council from the late Metropolitan Board of Words, is not greatly approved of. This might be expected, as the material used is lime in the proportion of 3·7 grains to 1 grain of copperas. Hence the effluent is of necessity alkaline.

The "amines process," or, as it is facetiously called, the herring-pickle method, is described at great length, but with the remark that it does not seem to be received with popular favour.

Webster's electrical treatment seemed to us very satisfactory when it was tried at Crossness. An electrical process, substantially the same, is now in use at Rouen and Havre, but the credit of its invention is not given to Mr. Webster.

General Scott's process, the subject of an endless series of patents, turned on precipitation with lime and clay. The effluent was of course alkaline. The deposit was ignited in kilns and sold as cement. It has been abandoned at Birmingham, since the nitrogen and the phosphates were wasted, and since the cement was neither better nor cheaper than that made in the ordinary way without the addition of sewage-matters.

Hille's process is said to be destructive of fertilising properties.

The Committee of the Local Government Board on Sewage Treatment (1875) are accused of pronouncing Goodall's process "the twin of the A B C process," and declaring both a failure. Both analysis and observation prove that the A B C process is here unfairly treated.

The process now in use at Coventry is no longer that of Anderson (phosphates), but lime and iron, followed by irrigation.

At Kettering, since the author obtained his information, the sewage is sterilised by the injection of carbolic and cresylic acids emulsified with steam. The sewage is then precipitated with salts of alumina. The process seems to give great satisfaction, and is being adopted at Melton Mowbray.

Mr. Wardle's work will, we believe, do good service.

*Dangerous Trades for Women.* By Mrs. C. Mallet. London: W. Reeves. Small 8vo., pp. 22. 1893.

This pamphlet forms one of a series of publications issued by the so-called "Humanitarian League." No one can be more fully convinced than are we that whatever tends to sap the health and the vigour of the community should be at once and thoroughly rectified. But whilst keeping in view Earl Beaconsfield's grand maxim "Sanitas sanitatum et omnia sanitas," we must all the more insist that existing evils should be stated truthfully, without either exaggeration or distortion. Their exposure must be conducted in the pure interest of public health, and not in the intention of making political or socialistic capital.

We are led to make this remark from a distrust of the spirit of this pamphlet and of the motives of the writer and of her associates. Those who really wish to know the truth, and nothing but the truth, concerning dangerous trades had better be guided by the discourses of Professor Watson Smith than by the sensational letters which appear in a certain class of papers. It is all very well to talk of the "ignorant carelessness of the masters." If Mrs. C. Mallet were really acquainted with her subject she would know that employers have often great difficulty in enforcing sanitary regulations in their establishments. The steel and stone dust which now no longer "surrounds the Sheffield cutlers" (it was not the cutlers but the grinders who were exposed to this evil) was got rid of by boxing in the revolving stones in sheet-iron jackets traversed by a strong current of air. But the workmen resisted this improvement, and even destroyed the apparatus.

As far as our opinion may have any weight, we hold most decidedly that the use of white-lead as a pigment should at all hazards be abolished. Nor do we think that the use of phosphorus at all, white or red, is a necessity. It is possible to make matches without its presence.

The author's appeal to the "Women's Liberal Associations of Great Britain" shows at once the political bearing of this pamphlet.

Some of the other publications of the League—such as No. 2, "A Denunciation of the Queen's Buckhounds"; No. 3, on "Rabbit Coursing"; No. 4, "The Horrors of Sport"; and No. 5, "Behind the Scenes in Slaughter Houses"—seem to deserve attention. But to "Humanitarianism" the League adds Bestiarianism, since one of the tracts deals with experimental physiology.

If they would denounce the massacre of harmless and beautiful birds at the behest of modistes they would be doing much better.

**The Use of the Electric Current as a Source of Heat in Dry Metallurgical Tests.**—W. Borchers (*Zeit. Angew. Chem.*).—The author points out the advantages of the current as a source of heat, and describes a kind of electric furnace.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

### *Zeitschrift fur Analytische Chemie.*
### Vol. xxxii., Part 4.

**A New Method for the Quantitative Determination of Carbon in Iron and Steel.**—Otto Pettersson and August Smith.—This paper, besides small figures introduced in the text, requires the two large plates at the end of the volume.

**Critical Studies on Methods for Determining Sulphur. (II.).**—L. Marchlewski.—The author examines the methods of Gröger or of Treadwell. He concludes that Gröger's method cannot be used commercially for the valuation of pyrites, and that it is unsuitable for determining sulphur in lead sulphate and analogous compounds. He is of opinion that Sawer's method cannot compete with that of Lunge in sulphuric acid works on account of the greater rapidity of the latter. But if a product has to be examined which contains along with pyrites other fixed and insoluble compounds, such as calcium sulphate, only the method of Sawer or the most recent modification of Treadwell's process can be used.

**Distinction between Natural Butter and Margarine.**—F. Gantter.—Already inserted.

**Valuation of Hides for Glue.**—F. Gantter.—Already inserted.

**A New Volumetric Method of Determining the Value of Fowler's Solution and Tartar Emetic.**—Dr. Stefan Györy.

**Standardising Acids by means of Metallic Sodium.**—Dr. Erich Neitzel.—A small beaker is filled to one-third with petroleum which has been heated above the boiling-ing point of water, filtered through paper, and tared on the balance. A rectangular piece of about 0·6 to 1 grm. in weight is then cut with a penknife from a rod of sodium, so that it has freshly-cut surfaces on all sides, taken up with the forceps, and allowed to slide into the beaker. On weighing again, the difference shows the weight of the sodium taken. The weighed portion is then taken up with the forceps, and without regard to the adherent petroleum allowed to slide into a flask holding from 250 to 300 c.c., and containing 75 c.c. of alcohol of from 88 to 94 per cent. The neck of the flask is then closed with a perforated cork or caoutchouc stopper, through the aperture of which is thrust a glass tube previously rinsed with alcohol. The development of hydrogen takes place quietly. After the completion of the reaction a few c.c. of alcohol are poured through a cooling tube into the flask, the stopper is rinsed off, and the contents of the flask are diluted with about 100 c.c. of distilled water. After adding phenolphthalein or some other indicator we may at once proceed to titration. The weight of the sodium increased by the factor—

$$\frac{1000}{23}$$

gives the consumption of the acid (supposed to be normal) in c.c. We may therefore at once allow three-fourths of the calculated number of c.c. to flow into the solution of sodium hydroxide, adding the remainder drop by drop until the change of colour takes place.

**Arrangements of the Electrolytic Laboratories of the Joint Stock Company at Stalberg, Westphalia.**—H. Nissenson and C. Rüst.—This paper requires the four accompanying figures.

**On Characterising Portland Cement.**—R. Fresenius and W. Fresenius.—The authors assign the following limits for the properties of Portland cement:—1. Specific gravity, not ignited, at least 3·00. 2. Specific gravity, ignited, at least 3·12. 3. Loss on ignition, at most 3·4. 4. Alkalinity of aqueous solution of 0·5 cement, not more than 7·2 c.c. of decinormal acid. 5. Consumption of permanganate for 1 grm. cement, not more than 2·8 m.g. 6. Proportion of magnesia, not above 3 per cent.

**General Process for Determining Foreign Bodies in Liquids.**—E. Gossart (*Chem. Zeit.*).—If a drop of a volatile liquid is caused to fall upon the surface of another liquid, curved by adhesion, if the drop and the subjacent liquid are both homogeneous it rolls for a time upon the lower liquid. But if the liquids are of unlike nature it sinks more or less rapidly into the lower stratum.

**A Method of Securing Riders on Artificial Balances.**—A. K. Markl.—This paper requires its three figures.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Cocoa-nut Oil.**—Will some correspondent kindly inform me—(1) What quantity and strength of soda ley is required to kill 1 cwt. of cocoa-nut oil for grease manufacture (not soap)? (2) What proportionate quantity of water will cocoa-nut oil carry as compared with palm oil?—J. I.

## MEETINGS FOR THE WEEK.

Friday, 24th.—Physical, 5. "On the Magnetic Shielding of Concentric Spherical Shells," by Prof. A. W. Rücker, M.A., F.R,S., President. "On the Action of Electromagnetic Radiation on Films containing Metallic Powders," by Prof. G. M. Minchin, M.A.

THE CHEMICAL NEWS.

Vol. LXVIII., No. 1774.

### ON THE
## TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Continued from p. 238.)

In order to secure a well arranged plan and to divide the material uniformly, certain rules must be followed to determine which constituent of a compound is to be spoken of and described. We have the option of treating the salts either in connection with the metals which are contained in them, or in connection with the acids. Berzelius, as is well known, has tried both methods, and in the later editions of his books first gives a survey of the characteristic properties of the acids, and then describes the individual salts according to the metals. Those who have studied Berzelius's method, or any similar plan arranged from the modern standpoint, must see that the enumeration of all its salts in connection with a metal forms, not only an arbitrary, irregular, and imperfect association of the most varying types and formulæ, but also necessitates innumerable repetitions which waste time, and are, moreover, wearisome to the student. However worthy of commendation this arrangement according to the metals may be for analytical chemistry, it is little adapted for a general course of experimental chemistry. The attributes of the salts of a metal can be well characterised without describing all the salts one after another. Further, isomorphism among large groups of salts can be produced just as well by the change of the positive as of the negative constituent; but metals of the different families may replace each other without change of crystalline form, whilst the negative elements of isomorphous compounds belong, with few exceptions, to the same family. From these and similar considerations, Professor Lothar Meyer decides on treating the salts always in connection with their acids. As, however, the hydracids of the type HCl and $H_2S$ have already been described, this rule is not made to extend to them, but only to the oxyacids and the sulpho-salts analogous to them.

After the occurrence, mode of extraction, and properties of the elements of each family have been spoken of, their compounds are discussed in the same order as those of hydrogen: first with Family VII., F, Cl, Br, and I; and then with Family VI., O, S, Se, Te, together with the oxides, hydrates, and also the sulphydrates. When they are of importance, the compounds with Family V., N, P, &c., and also with Family IV., C, Si, &c., are also treated. In this way, the position in the system of every compound is definitely determined. This uniformity does not, of course, compel a like treatment for all sections, but allows full freedom to discuss the more important in detail, whilst the less important are either only briefly mentioned or are omitted altogether.

Professor Meyer was formerly in the habit of introducing with the purely empirical discussion of each family the general formula of its compounds, and, from it, of deducing its valency, so as, by induction, to lead up to the knowledge of the general law. But, as he has noticed in the course of time, that the tendency in preparatory schools is to induce the student to assimilate the lecture-course more by memory than by reasoning, he now follows a more deductive and dogmatic procedure, and accordingly gives for every family first of all its typical formula, according to which its compounds are formed—as, for example, the alkali metals:—

I.—RCl, $R_2O$, ROH, $R_2S$, RSH, &c.,

and for the metals of the alkaline earths:—

II.—$RCl_2$, RO, $RO_2H_2$, RS, $RS_2H_2$, &c., &c.,

so that, in this way, the student knows what to expect; and at the same time proofs are given for using for calcium chloride $CaCl_2$, instead of Gmelin's formula CaCl.

Professor Lothar Meyer begins his systematic consideration with the Family of the alkali metals, taking the opportunity to introduce instructive incidents in the history of chemistry as well as explanations of important methods of research. Electrolysis, the stoichiometric determination of atomic and equivalent weights, acidimetry, and alkalimetry are demonstrated and described.

Attention is especially called to the increase of the positive character of the elements with the increase of atomic weight. From its association with the alkalis, ammonia is again referred to, its salts and their isomorphism with the potassium salts spoken of; and mention is now made of the compound salts, those of ammonia being particularly dealt with.

Family II. of the earth-metals — beryllium, magnesium, calcium, strontium, and barium — is so nearly analogous to Family I. that a brief comparison is sufficient. After the discovery, occurrence, and mode of extraction have been spoken of, special emphasis is laid, when describing their properties, on specific heat and on the law of Dulong and Petit, from which the divalency of the Family is inferred. Beryllium gives occasion to explain the exception to this law, and to deduce the proof of the divalency of the metal from the vapour-density of the chloride. As divalent bases, the hydrates offer opportunity to discuss the relations of equivalent to atomic weight, and to differentiate between them. Here, again, the increase of the positive character with atomic weight is noted. As types of intra-reaction with Family I., the preparation of the alkaline hydrates by means of those of the alkaline earths, as well as of the reverse operation, is experimentally shown. The peroxides are also discussed, especially barium peroxide; and, in addition, the earlier-mentioned hydrogen peroxide. With the sulphides the phosphorescent compounds are shown.

Family III. — boron, aluminium, scandium, yttrium, lanthanum, and the others for the most part grouped with the indefinite earth-metals — is conveniently treated in a somewhat different way. The type of compound is alike for all; but the properties of boron and its compounds differ so much from the others, in spite of their analogous composition, that it is advisable to describe them alone, and before the others. Boracic acid, or the trihydrate $BO_3H_3$, manifests such a great diminution of basic and positive character, as compared with LiOH and $BeO_2H_2$, that it is classed as a weak acid capable of forming salts. The weakness of the acid is shown in the decomposition of the borates by water, and in the formation of the anhydrous salts $BO_2Na$, $B_4O_7Na_2$, &c. The latter compound is more particularly described as a type of a frequently recurring phenomenon, so that later, or when a similar compound is formed in connection with other acids, it need only be mentioned.

Of the metals of this Family, aluminium is especially considered, and allusion is made to the analogies its compounds show to those of boron—particularly the chloride and hydrate with its weak acidic nature. The very rare members are briefly treated; at the same time it is mentioned that cerium in Family IV. is nearly related to lanthanum, and apparently all the insufficiently known elements between lanthanum and barium have the character of earth-metals. Whether didymium should be placed in Family V. is somewhat doubtful. Owing to the great similarity of these earth-metals to one another, it is convenient to discuss them all now, so far as this can be done in an elementary course.

As occasion offers during the consideration of this Family, as well as those preceding and following it, it is remarked that the elements of low atomic weight, as lithium, beryllium, and boron, occur but seldom; those of higher weight to perhaps iron (at. wt. =56), are, without exception, frequently and widely distributed; whilst all of higher weight than iron are much more rarely found on the earth's crust.

The elements of Family IV.—carbon, silicon, titanium, zirconium, cerium, thorium—are described together, by reason of the similarity of their properties, their occurrence, and modes of preparation. But the compounds of carbon exhibit such marked differences from those of the others that they are especially dealt with.

Of the halogen compounds of carbon only those of the type $CCl_4$ are somewhat minutely described, the others being merely mentioned, and their fuller treatment referred to organic chemistry. The oxides of carbon are discussed in detail—particularly carbonic acid as well as its salts. The consideration of the carbonates gives occasion to compare them with the borates of Family IV. Since the normal hydrate of carbon should be $CO_4H_4$, all carbonates appear as anhydrous salts of the type $CO_3H_2 = CO_4H_4 - H_2O$. They are treated in groups, at first with the alkalis, then with the great isomeric family of calc-spars and aragonites, and of others allied to them so far as they are worthy of consideration. After carbonic acid, carbon monoxide, carbon bisulphide, phosgene, and urea are discussed briefly, the associated carbamic acid having been already shown and explained when dealing with the carbonates of the alkalis. Finally, the compounds of carbon and nitrogen are dealt with.

The compounds of the remaining elements of Family IV. are next described, first the fluorides, chlorides, &c.; then the oxides and hydrates, or anhydrides and acids. The silicates furnish numerous examples of the anhydrous salts of the polysilicic acids, which are grouped and characterised according to the type of metal with which they combine. As silicates, pottery, porcelain, and glass are here mentioned. Titanium, zirconium, and thorium are only briefly treated. Whether cerium really belongs to this Family remains doubtful; it has, however, been already spoken of.

Between Families IV. and V. a peculiar and sudden change of properties is manifest. From the hitherto infusible carbon we come to the gaseous and, up to now, difficult to liquefy nitrogen, and from the very difficultly fusible silicon to the easily-fused phosphorus. All the previously considered elements, moreover, have been distinguished by their great affinity for oxygen, all being difficult of reduction. This property is seen also in phosphorus, but not in nitrogen, whose oxides, as is known, readily yield oxygen. In comparison with titanium and zirconium we have vanadium and niobium, to which, as third member, tantalum is associated, whose analogue in Family IV. is yet to be discovered. If we include Family VI. we have the following grouping:—

| | | |
|---|---|---|
| C = 11·97 | N = 14·01 | O = 15·96 |
| Si = 28·3 | P = 30·96 | S = 31·98 |
| Ti = 48·0 | V = 51·1 | Cr = 52·0 |
| Zr = 90·4 | Nb = 93·7 | Mo = 95·9 |
| — | Ta = 182·0 | Co = 183·6 |
| Th = 231·9 | — | U = 238·8 |

(To be continued).

**Burettes and Pipettes.**—A number of proposals put forward, for the most part merely slight modifications of forms already known. G. A. Le Roy (*Moniteur Scientique*) describes an overflow burette and pipette, in which the zero-point of the graduation coincides with the upper end. The burette is filled from an elevated reservoir by means of a T-piece ⊢. The liquid running out above arrives into a glass jacket, inclosing the burette for its whole length and having at its lower end a lateral escape-pipe. The inclosure of the entire burette in a glass-jacket must certainly render the reading off less accurate.—*Zeitschr. Anal. Chem.*, xxxii., Part 4.

# THE ELECTROLYTIC SEPARATION OF THE METALS OF THE SECOND GROUP.*

By SAMUEL C. SCHMUCKER.

(Concluded from p. 245).

### *Bismuth from Arsenic.*

The solution was made by dissolving 5·8 grms. of bismuth nitrate in water acidulated with enough nitric acid to prevent the formation of basic salts. The solution was diluted to 400 c.c., and ten c.c. taken for the determination of the bismuth. The metal was precipitated from the alkaline tartrate solution and weighed 0·0518 grm. The practice had now become uniform of adding 5 grms. of tartaric acid and 15 c.c. of ammonium hydroxide when two metals were present, and 8 grms. of acid and 30 c.c. of ammonium hydroxide when four metals were in the same solution. The solution was made up as in all preceding cases, and the process differed in no way until the washing began. Bismuth does not form so compactly on the dish as cadmium does, or even as copper from the alkaline tartrate solution. Accordingly great care was necessary in the washing. In drying, too, it seemed to oxidise with very little heating. Therefore, when the deposition was complete, the anode was raised, the liquid gently but quickly decanted from the deposited bismuth, and the wash-water gently poured on and off. This latter was repeated three or four times, and was followed by three or four washings with absolute alcohol. The dish was placed on a very moderately heated plate and the evaporation of the alcohol facilitated by gentle blowing. It is best to use a long-continued weak current for bismuth or the deposit will be spongy and loose, rendering washing difficult.

*Experiment* 1.—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0·1009 grm. metallic arsenic, and 0·0518 grm. of bismuth. It was diluted to 175 c.c. The current acted sixteen hours and gave 0·3 c.c. of electrolytic gas per minute. The precipitated bismuth weighed 0·0514 grm.

### *Bismuth from Antimony.*

Here the procedure was exactly similar to that described under the separation of bismuth from arsenic. The precipitated metal resembled that obtained in the preceding experiment.

*Experiment* 1.—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0·1024 grm. of antimony, and 0·0518 grm. of bismuth. It was diluted to 175 c.c. The current gave 0·22 c.c. of electrolytic gas per minute. It acted sixteen and one-half hours. The deposit of metallic bismuth weighed 0·0513 grm.

### *Bismuth from Tin.*

The method of procedure was just the same here as in the separation of antimony, or of arsenic from bismuth. The precipitated bismuth was treated as heretofore and had the same appearance.

*Experiment.*—The solution contained 5 grms. of tartaric acid, 15 c.c. of ammonium hydroxide, 0·1031 grm. of metallic tin, and 0·0518 grm. of metallic bismuth. It was diluted with distilled water to 175 c.c. The acting current gave 0·2 c.c. of electrolytic gas per minute; time, sixteen and one-half hours. The bismuth deposit weighed 0·0514 grm.

### *Bismuth from Arsenic, Antimony, and Tin.*

The procedure was again just as before. The bismuth precipitated readily and in as clean a form as when separated from each of the metals singly.

*Experiment.*—The solution contained 0·0518 grm. of bismuth, 0·1009 grm. of arsenic, 0·1024 grm. of antimony,

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* From the *Journal of the American Chemical Society*, vol. xv., No. 4, 1893.

0·1031 grm. of tin, 8 grms. of tartaric acid, 30 c.c. of ammonium hydroxide, and was diluted to 175 c.c. The current gave 0·2 c.c. of electrolytic gas per minute, and was allowed to act for sixteen and one-half hours. The bismuth, after washing and drying, weighed 0·0513 grm.

The method adopted by me having proved successful in the separation of copper, cadmium, and bismuth from the metals forming acid oxides, I next applied it to the study of mercury in its bivalent form. About 7 grms. of mercuric chloride were dissolved in distilled water and diluted to 500 c.c. Ten c.c. of this solution proved to contain 0·0933 grm. of metallic mercury. I first undertook the separation of—

### *Mercury from Tin.*

There was a doubt in my mind whether the mercuric compound could be made up in alkaline tartrate solution when there was so much free ammonia present. I found, however, that if the mercuric chloride solution be added to the tartaric acid solution before the addition of the ammonia there is little likelihood of trouble, though even then the double compound sometimes forms, especially if the solution be not dilute. But if care be exercised the mercuric salt may be added last. If the solution is well diluted and the mercuric salt added with constant stirring all remains in solution very nicely. The mercury and tin were then combined with the tartaric acid and ammonia, the solution diluted and the current passed. The precipitation is quite rapid even with a fairly weak current, and the metal separates as a lustrous coating having a very slight tendency to drops. The mercury is washed with very warm water three or four times, and then dried by keeping the dish in the warm hand and blowing gently into it to facilitate the evaporation. Any attempt to dry it on the plate is attended with very considerable risk of vaporising a portion of the mercury.

*Experiment.*—Ten c.c. of the mercuric chloride solution (=0·0933 grm. metallic mercury, 10 c.c. of tin solution, 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide) were united and diluted to 175 c.c. The current gave 0·2 c.c. of electrolytic gas per minute and was continued for six hours. The mercury deposited weighed 0·0930 grm.

### *Mercury from Arsenic.*

The solution contained 0·0933 grm. of mercury, 0·1009 grm. of arsenic, 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide. It was diluted to 175 c.c. The current gave 0·33 c.c. of electrolytic gas per minute, acted for five hours, and deposited 0·0928 grm. of metallic mercury.

### *Mercury from Antimony.*

*Experiment.*—The solution contained 0·1024 grm. of antimony in addition to the mercury, also 5 grms. of tartaric acid, and 15 c.c. of ammonium hydroxide. It was diluted to 175 c.c. with water. The current gave 0·5 c.c. of electrolytic gas per minute; it acted for six hours, and precipitated 0·0932 grm. of metallic mercury.

### *Mercury from Arsenic, Antimony, and Tin.*

The solution was made up in the same manner as in the three preceding separations, save for the increase of tartaric acid and of ammonium hydroxide. There was, however, a difference in the nature of the deposited mercury. A part of it gathered, as in the other cases, in a lustrous coating on the sides of the dish, but in addition to this there was quite a considerable amount of mercury in the form of drops so small as to be almost pulverulent. This rendered washing exceedingly difficult. The fluid contents of the dish, after the anode had been raised, are carefully decanted from the powder, boiling water added, allowed to flow around the dish, and again very carefully decanted. This was repeated six or seven times, never draining off the last drops to avoid loss of the mercury. If this care is taken there is no difficulty about good results, but the slightest haste results in the loss of mercury. Naturally when that much water remains on the mercury the evaporation from the heat of the hand is a most tedious, but the only safe, process.

*Experiment* 1.—The solution contained 0·0933 grm. of mercury, 0·1009 grm. of arsenic, 0·1024 grm. of antimony, 0·1031 grm. of tin, 8 grms. of tartaric acid, 30 c.c. of ammonium hydroxide, and was diluted to 175 c.c. The current gave 0·5 c.c. of mixed gases per minute. It acted for sixteen hours and precipitated 0·0935 grm of mercury.

*Experiment* 2.—The conditions were the same as in the first experiment. The current gave 0·4 c.c. of electrolytic gas per minute and precipitated 0·0933 grm. of metallic mercury.

I made no attempt to separate lead from arsenic, antimony, or tin.

In conclusion, I would acknowledge my indebtedness to Prof. Edgar F. Smith, at whose suggestion and under whose supervision the above studies were brought to completion.

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## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending October 31st, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

*To* Major-General A. De Courcy Scott, R.E.,
*Water Examiner, Metropolis Water Act*, 1871.

London, November 10th, 1893

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 2nd to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

A comparison of the average composition of the five Thames-derived waters during last month with that of the same waters in October, 1892, shows a decided improvement in the amount of nitrates, in the oxygen required to oxidise the organic matter, and in the organic carbon. Notwithstanding a somewhat heavy rainfall, the composition of the waters during the last month is almost identical with that recorded in September, when the Thames waters were of a wholly exceptional degree of purity, the increase in organic carbon in October over that in September only amounting to one part in seven million parts of water, as will be seen by the following Table:—

*Averages of the Five Supplies derived from the River Thames.*

| 1893. | Common salt per gallon. | Nitric acid per gallon. | Hardness, degrees. | Oxygen required per gallon. | Organic carbon per gallon. | Organic carbon per gallon. | Colour. | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Brown. | Blue. |
| | Means. | Means. | Means. | Means. | Means. | Maxima. | Means. | |
| Sep. | 2·163 | 0·570 | 13·64 | 0·026 | 0·057 | 0·071 | 12·2 : | 20 |
| Oct. | 2·197 | 0·665 | 14·10 | 0·031 | 0·067 | 0·099 | 13·8 : | 20 |

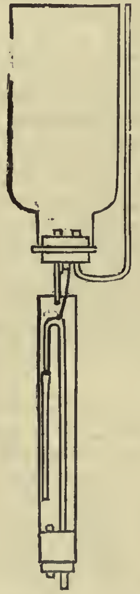
The rainfall in the month of October at Oxford[*] was very near the mean fall for the month over an average of twenty-five years. The actual fall was 2·65 inches, while the mean is 2·56 inches. Most of the rain occurred in the early part of the month, 1·9 inch, or 72 per cent, falling in four days. Although this heavy rain immediately followed an exceptionally dry month, the self-purifying power of the running stream and the aërating and filtering arrangements of the Companies have proved amply sufficient to prevent any rise in organic matter, our analyses showing no variation in the uniform good quality of the water between the first and the second half of the month.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## AN AUTOMATIC EXTRACTOR.

By W. D. HORNE.

In the analysis of commercial fertilisers soluble phosphoric acid is separated by repeated washings of the mass with small quantities of water. Two grms. of the sample are treated on a ribbed filter with successive portions of water, about 10 c.c. at a time, until at least 250 c.c. have run through, each addition being deferred until the preceding has passed through.



Feeling that time might be saved by having this washing done automatically led to the device of a simple apparatus which mechanically delivers the required quantity of water at measured intervals in a gentle stream upon the material on the filter, stirring it up and leaching out the soluble matter without requiring any attention after the start.

One part of the apparatus consists of a wide-mouthed bottle of 250 c.c. capacity closed by a cork perforated by two glass tubes. One tube projects outward about 3 or 4 c.m. and tapers to a moderately fine point. The other tube, after emerging from the cork, curves directly over the edge of the cork and extends down the full length of the bottle on the outside. The bottle, being filled with water, is inverted, and the water drops from the end of the short tube, while the necessary air enters by the long bent tube, and bubbles up through the column of water in the bottle. As the rate of flow or dropping depends principally upon the fineness of the point of the dropping tube and the freedom of the air's access through the longer tube, any desired rapidity of flow can be obtained by varying the size of either tube. It is more advantageous to use the same dropper and to regulate the air supply by plugging more or less loosely the upper end of the air tube with an appropriate stopper.

So much for the water supply. In order to convert this into an intermittent washing stream it flows into a tube suspended below, provided with a capillary syphon tube within, whose longer limb passes through a stopper at the bottom of the outer tube, something like the Adams fat extractor.

To make this part of the apparatus, cut the bottom off of a test-tube 15 m.m. in diameter and 15 c.m. long, close one end with a rubber stopper with one hole, and within the test-tube put a 3 m.m. tube bent double by a sharp curve, with one limb about 15 c.m. long and the other about 3 c.m. The longer limb passes through the hole in the stopper at the bottom of the test tube, while on the shorter limb is put a piece of rubber tubing of variable length, according to the quantity of water that is to be syphoned off at each delivery. To the loop of the syphon fasten one end of a short wire, whose other end terminates in a hook to catch in a wire eye inserted in the cork of the inverted bottle.

Thus suspend the syphon apparatus to the water supply, having the dropping-tube inside the test-tube. When the water is allowed to drop the test-tube slowly fills, until the water, rising in the syphon's short arm, passes beyond the bend and syphons over. The operation then repeats itself.

The speed of dropping from the reservoir must be such as to allow each syphoned portion to pass completely through the filter before the next flows on. And the quantity which syphons over each time is to be regulated by varying the length of the rubber tube which extends from the short limb of the syphon. The lower end of this rubber tube is cut off diagonally to ensure complete emptying of the syphon at each delivery.

These things once arranged, they need little attention afterwards.

Only a moment is required to fill the bottle, attach the syphon tube, and hang the inverted bottle in its rack with the filter containing the fertiliser below it in a funnel resting in a flask.

The washing is done regularly, without attention and without loss of time. A few supplementary washings by hand may be well to get the material all into the point of the filter, although experiments have shown that the mechanical washing is thorough and gives results identical with the tedious hand method.—*Journal of the American Chemical Society*, xv., No. 5.

## ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.[*]

By THEODORE WILLIAM RICHARDS and ELLIOT FOLGER ROGERS.

(Concluded from p. 242).

### *Nickelous Oxide.*

The series of experiments with nickelous oxide led to results not unlike those with zincic oxide. In this case sulphuric acid proved unsatisfactory as a solvent, and

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[*] Oxford has been chosen in preference to London, as its rainfall more closely represents the average fall over that part of the gathering ground of the Thames valley which supplies the chief sources of the river.

[*] Contributions from the Chemical Laboratory of Harvard College.

hydrochloric acid was adopted. A solution containing about 20 per cent of hydrochloric acid gas was freed from air by continued boiling, rapidly cooled, and run into the tube containing the oxide of nickel. On account of the very slow action of the cold acid the tube was warmed after exhausting the air as usual. The gas set free was measured as before.

In order to prove the accuracy of the method a grm. of zincic oxide prepared from the carbonate was dissolved in hot hydrochloric acid in precisely a similar way. No trace of gas was evolved during this solution.

It was thought unnecessary to make a series of experiments as elaborate as that made with the zincic oxide. Nickelous nitrate was evaporated to dryness in porcelain and ignited 15 minutes in a blast lamp and then a number of hours over a Bunsen burner in the furnace. (Analysis 1, below).

A part of the nickelous oxide remaining was further ignited for two hours in the furnace by means of the water-blast. This was used for the second analysis. A portion of the latter was ignited again in the furnace at the highest temperature we could obtain, by the addition of oxygen to the flame for about 15 minutes, until the bottom of the outer crucible as well as the platinum foil between the two crucibles was melted away. The arrangement of data in the Table is similar to that already described.

| No. of Expt. | Weight of Oxide. | Vol. of Gas evolved. | Vol. of Gas calc. for 10 gr. NiO. | Analysis of Gas by volume. |
|---|---|---|---|---|
| | Grms. | C.c. | C.c. | Per cent. |
| 1. | 1·14 | 0·469 | 4·11 | $O_2 = 12·25$<br>$N_2 = 87·75$ |
| 2. | 0·997 | 0·34 | 3·41 | |
| 3. | 1·13 | 0·35 | 3·09 | $O_2 = 8·8$<br>$N_2 = 81·2$ |

### *Magnesic Oxide.*

The experiments with the oxide of magnesium led to very unexpected results, the amount of gas evolved upon the solution of this compound being five to twenty times as much as was obtained from zincic oxide, and over twenty-five times as much as from the oxide of nickel. More difficulty was found in decomposing the nitrate than before, and the remaining oxide was in a much harder and more compact state, and consequently more difficult to pulverise. The process used was similar to that employed in the case of the other oxides.

| No. of Expt. | Wt. of Oxide used. | Time and Temp. of heating. | Vol. of Gas evolved. | Vol. of Gas calc. for 10 gr. of MgO. | Analysis of Gas. |
|---|---|---|---|---|---|
| | Grms. | | C.c. | C.c. | |
| 1. | 0·50 | Blast lamp 30 mins. | 5·45 | 109· | $O_2 = 66·6\%$<br>$N_2 = 33·4$ |
| 2. | 1·0 (about) | ,, 1 hr. | 0·05 | 0·5 | |
| 3. | 0·50 | ,, 1¼ ,, | 5·86 | 117·2 | $CO_2 = 5·98$<br>$O_2 = 53·7$<br>$N_2 = 40·29$ |
| 4. | 0·25 | ,, 2¼ ,, | 2·31 | 92·4 | $O_2 = 47·6$<br>$N_2 = 52·4$ |
| 5. | 0·25 | ,, 3¼ ,, | 2·31 | 92·4 | $CO_2 = 2·2$<br>$O_2 = 38·9$<br>$N_2 = 58·9$ |
| 6. | 0·25 | Oxygen blast, 20 mins. | 2·04 | 81·6 | $O_2 = 34·3$<br>$N_2 = 64·2$<br>$CO_2 = 1·5$ |
| 7. | 0·25 | Water blast, 1½ hr. | 2·31 | 92·4 | |

*Remarks.*

*No.* 2.—Made from carbonate.

*Nos.* 3 *to* 6.—Analyses made from one sample of oxide heated under different conditions. 1, 3, and 4 gave tests for nitrates with ferrous sulphate; 5 and 6 did not.

Magnesic nitrate made from pure nitric acid and magnesic carbonate of commerce was evaporated to dryness in porcelain. The residue was pulverised in an agate mortar, heated by means of the blast lamp in a covered porcelain crucible, and cooled over calcic chloride. For a parallel experiment, a portion of the original carbonate was converted into the oxide by simple ignition, the magnesia formed in this way evolving only an extremely small amount of gas upon solution (Expt. 2).

A third portion of magnesic nitrate was made from pure magnesium ribbon and pure nitric acid, and the oxide was obtained from this salt by evaporation and ignition in porcelain as usual (Expt. 7).

Sulphuric acid was used for the solution of the magnesic oxide, as in the case of zincic and cupric oxides. The preceding Table explains itself.

The amount of gas occluded by magnesic oxide is thus far more than that occluded by the oxides of copper, zinc, and nickel. The quantities of carbon dioxide recorded in the Table are undoubtedly far from accurate, since the gas was collected over water. It is interesting to note that the amount of nitrogen evolved by the oxide upon going into solution was slightly increased up to a certain point by the increasing time and heat of the ignition, while the amount of oxygen was rapidly diminished.

| No. of Expt. | Vol. of Nitrogen found in 1 grm. of MgO. | No. of Expt. | Vol. of Oxygen found in 1 grm. of MgO. |
|---|---|---|---|
| | C.c. Gas. | | C.c. Gas. |
| 1. | 3·6 | 1. | 7·2 |
| 3. | 4·72 | 3. | 6·3 |
| 4. | 4·84 | 4. | 4·4 |
| 5. | 5·44 | 5. | 3·6 |
| 6. | 5·24 | 6. | 2·8 |

### *The Oxides of Cadmium, Mercury, Lead, and Bismuth.*

These oxides, the only other suspected ones which could be easily analysed by the method in hand, all yielded negative results. The oxide of cadmium was distinctly crystalline, and contained only the merest trace of gas. The oxides of mercury, lead, and bismuth obtained by the ignition of the corresponding nitrates also appeared to contain no occluded gaseous impurity.

Unfortunately the oxides of antimony, iron, and a number of other metals are not sufficiently soluble in acids to test with ease their power of occlusion by this method. It seems probable that interesting results might be obtained from them; hence in the near future other methods will be tried here, with the hope of determining if these oxides also occlude gaseous impurity.

### *Theoretical Considerations.*

From the fact, observed with both copper and zinc, that oxides which still contain a trace of nitrates, as well as those made from the carbonate, retain no imprisoned gas, it is readily inferred that the decomposition of a trace of nitric acid is alone responsible for the impurity. It is natural that this last trace of nitric acid should be confined below the surface, whence the gases resulting from its ultimate decomposition would find it hard to escape. On this supposition it is not unnatural that zincic oxide which has been partly reduced, and hence somewhat disintegrated, should contain less occluded gas than that which has not been thus reduced. Moreover, since magnesic nitrate is harder to decompose than the other nitrates, and the oxide is more compact, we should expect to find more gas occluded in this case than in the others. All these inferences agree with the facts. The difference in the rate of expulsion of the oxygen and of the nitrogen is interesting and less easy to explain.

The negative results observed with a number of metals lead one to conclude that the physical condition of the oxides in these cases was so porous that even the last traces of nitrogen were allowed to escape. Indeed, cupric and zincic oxide made from very finely divided basic nitrates, obtained from aqueous solution, contained much less gas than samples which were obtained in a more compact condition by the direct ignition of the normal nitrate. This fact shows how much depends upon physical conditions.

It must be borne in mind that the occlusion of gases noted in this paper is a very different phenomenon from the retention of undecomposed oxides of nitrogen alluded to by Marignac,[*] Morse and Burton, and others. Nitrogen present in the state of gas could of course give no test with sulphanilic acid and naphthylamine, or any other test for oxidised nitrogen. It is evident that the phenomenon we are now studying, like the other just spoken of, may be a very serious cause of error in many of the published determinations of atomic weights; these would hence appear lower than their true value, because of the extra material which is calculated as oxygen.[†] Before any quantitative results obtained in this way can be accepted as authoritative, definite proof must be brought forward of the absence of this source of error. It is to be hoped that the able experimenters who have recently worked upon zinc, nickel, magnesium, and similar metals, have preserved typical specimens of their final products. If this is the case, nothing could be easier than to determine the amount of occluded gas, if any is present, and to apply the necessary correction.

As long ago as 1887 one of us was engaged, through the suggestion of Professor Cooke, upon an investigation of the atomic weight of zinc depending upon the analysis of zincic bromide. The work was discontinued because of the many publications upon this subject which appeared before it could be completed. Since the results recorded in this paper appear to indicate that the last word has not yet been said upon the subject, the investigation of zincic bromide and chloride is now being continued in this Laboratory.

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## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.[‡]

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 240).

THAT my expectations depending on the greater transparence of fluorite were realised only to a limited extent in that part of the spectrum which has been already observed with quartz, and in the region beyond it not at all, may be here mentioned only in a preliminary manner, and because the following proofs might otherwise readily lead to erroneous conclusions.

B. *In Dry Gelatin.*—In principle and in arrangement the experiment resembled the foregoing. Much time was taken up with the production of the gelatin film, the absorption of which was to be determined.

Soret made use of a watery solution of gelatin, which he placed between the slit and the source of light in a closed trough with parallel sides of quartz; a means equally convenient and certain of obtaining gelatin media of every desired thickness, but applicable only when the presence of water does not interfere. Water, even if recently distilled, is not indifferent in its behaviour with the most refrangible rays. When Soret placed in the track of the rays a trough of 10 m.m. in width, the line No. 32 disappeared entirely; whilst after emptying the trough, when there remained merely the absorption of the two quartz sides, it was visible again (*Archives des Sci. Phys. et Nat.*, vol. lxi., p. 336, 1878). For my purpose, therefore, the use of gelatin in solution was not admissible.

I made use of dry films of gelatin, which I made from a solution of gelatin in water. The stouter films of 0·1 m.m. in thickness and upwards were used without support, but the thinner films were placed upon a plate of quartz parallel to their plane. My observations were limited to thicknesses of gelatin suitable for silver bromide gelatin. But attention was principally given to such thicknesses as probably occur between the several particles of silver bromide of the coating of the plate.

We calculate in practice for a plate of 13 and 18 c.m. side-lengths and 10 c.m.$^3$ of emulsion fit for pouring, which contained in 100 parts by weight of water 5 parts by weight of gelatin. According to this proportion I covered with a 5 per cent solution of gelatin a plate of quartz placed in a level position. This plate was subsequently used for all films, and also for taking the absorption spectra. I dried it carefully, and then measured the gelatin film which I had taken off the middle of the plate with a micrometer capable of showing 0·01 m.m. From a number of measurements the thickness was found to be 0·020—0·021 m.m., which agreed well with measurements made on emulsion plates by others. On this thickness, which for the sake of simplicity I will assume as 0·020 m.m., is founded the thickness of all the thinner films, which will be referred to below. I did not disguise to myself the fact that the method, according to which I have determined here and subsequently the thickness of the films, might be open to various objections, but I held the degree of accuracy thus obtained completely sufficient for the purpose in view. I then made solutions containing in 100 parts by weight of water 2·5, 1, 0·5, 0·125, 0·100, 0·063, 0·100, 0·063, 0·004, 0·002 parts by weight of gelatin (Heinrich's hard emulsion gelatin). I poured with a pipette containing 1 c.m.$^3$ up the above-named quartz plate the same quantity as before, and spread the solution uniformly to the edge of the plate by means of a thin glass rod. The coating was dried in heat, and without any current of air, which, as I had ascertained in preliminary experiments, gives in solutions poor in gelatin layers which become thicker towards the middle of the plate.

The moistened plate, which had previously been carefully levelled, lay on a plate of mirror glass, which rested a few m.m. above the water-surface of a hot water-bath, and rested on the edge of the vessel. Above, on the plate of glass, there stood a spacious metal pipe open at both ends and several c.m. high, closed above with a second glass plate. The coating of the quartz plate dried consequently in an atmosphere of watery vapour. For the escape of the steam, the loose connection between the pipe and its glass cover was sufficient. The thickness of the films thus obtained was, on the basis of the above-made assumption, 0·010, 0·004, 0·002, 0·001, 0·0005, 0·0004, 0·00025, 0·00008, 0·00004 m.m. I laid bare the dried plate in its middle by means of a clean cut for some m.m. in length, and placed it in the camera in such a manner that the slit was covered for half its length with the coated plate, and for the other half for the part of the plate which had been laid bare. Each exposure then gave two spectra, and the difference between the two corresponded to the absorption of the gelatin film. As the source of light there were used Leyden jar sparks of cadmium, zinc, aluminium, thallium, and tungsten. The exposure began with a single spark (opening spark), and was never continued longer than three minutes. The plates this time were those of Dr. Schleumer, of Frankfort-on-Main; the development was as before. The proofs (276) were distributed on 60 plates.

(To be continued.

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[*] "Il est probable que l'oxyde de zinc et la magnésie ne sont pas les seuls oxydes qui retiennent aussi énergiquement des composés nitreux, lorsqu'on les prépare par la calcination de leurs azotates."—*Annales de Chimie et de Physique*, Series [6], i., p. 311, footnote.

[†] The following are the metals whose atomic weights have been determined by means of the oxide made through action of nitric acid:—Hydrogen (cupric oxide), Magnesium, Aluminium, Vanadium, Manganese, Nickel, Cobalt, Copper, *Zinc*, Gallium, Selenium, Tin, Antimony, Tellurium. See Meyer and Seubert, "Atomgewichte," pp. 17 to 42; also "Nickel," Krüss, *Zeit. Anorg. Chem.*, ii., 235; "*Zinc*," Morse and Burton, *Amer. Chem, Journ.*, x., 311—321; "Magnesium," Burton and Vorse, Chem. News, lxii., p. 267.

[‡] From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

The following are abstracts of papers received during the vacation, and published in the *Transactions*:—

56. "*Peri-derivatives of Naphthalene.*" By R. Meldola, F.R.S., and F. W. Streatfeild. (*Trans.*. 1893, 1054).

A description is given of the preparation of 1 : 1′-, or peri-nitronaphthylamine by nitrating α-naphthylamine in presence of sulphuric acid, and of the preparation from this compound of benzylidene-1 : 1′-nitronaphthylamine, 1 : 1′-nitrobromonaphthalene, 1 : 1′-bromonaphthylamine, 1 : 1′-bromonaphthol, and 1 : 1′-dibromonaphthalene.

57. "*Note on Lead Tetracetate.*" By A. Hutchinson, M.A., Ph.D., and W. Pollard, B.A. (*Trans.*, 1893, 1136).

It is shown that the compound which crystallises from a solution of red lead in glacial acetic acid, described by Jacquelain, in 1851, is *lead tetracetate*, $Pb(C_2H_3O_2)_4$. A corresponding propionate has been obtained. On adding ammonium chloride to a solution of the tetracetate in chlorhydric acid, a precipitate of the characteristic double salt of ammonium chloride and lead tetrachloride is produced.

58. "*Resolution of Lactic Acid into its Optically Active Components.*" By T. Purdie. Ph.D., B.Sc. (*Trans.*, 1893, 1143).

Inactive lactic acid has already been resolved into its active components by two of the three general methods discovered by Pasteur, namely, by selective fermentation, and by crystallisation of salts of the alkaloids. The author finds that the third method, that of spontaneous resolution by crystallisation, can also be applied with success.

In the course of an investigation on the resolution of lactic acid into its active components by crystallisation of the strychnine salts (Purdie and Walker, *Trans.*, 1892, 754) an active zinc ammonium lactate was encountered, which possessed in a marked degree the property of forming supersaturated solutions when dissolved in a syrup of active ammonium lactate, and of separating from these solutions in comparatively large, well-defined crystals. It was also observed that a strong solution of ordinary ammonium lactate dissolves large quantities of ordinary zinc lactate, forming a syrup from which an inactive zinc ammonium lactate does not at once crystallise, but which readily deposits zinc lactate when slightly diluted. These observations suggested the idea that possibly the active double salts might be present in such a solution in a state of supersaturation, and that they might be separately crystallised from it under suitable conditions of temperature and concentration by adding the proper crystalline nuclei.

It is found that by heating a solution containing certain definite proportions of ammonium lactate, zinc lactate, and water, and then cooling, a supersaturated solution is obtained, from which either of the active salts or the inactive salt can be separated at will by adding traces of the respective salts as nuclei. By alternately dropping into such a solution dextrogyrate and lævogyrate nuclei, and adding fresh inactive zinc lactate to the exhausted mother-liquor, it is possible to obtain successive crops of the oppositely active salts in quantity. By re-crystallisation, products are readily obtained containing over 90 per cent of the active substances. The admixture of inactive salt can be eliminated by crystallisation of the zinc lactate prepared from the double salts. Determinations of the specific rotations of the zinc lactates thus obtained gave numbers agreeing with those given by Wislicenus for zinc sarcolactate at similar concentration. When equal quantities of 8 per cent solutions of the oppositely active zinc ammonium salts are mixed, inactive zinc lactate is precipitated. The inactive zinc ammonium salt was also prepared, and was found to have the composition represented by the formula—

$$Zn(C_3H_5O_3)_2{\cdot}NH_4{\cdot}C_3H_5O_3{\cdot}3H_2O,$$

while that of the active salts is—

$$Zn(C_3H_5O_3)_2{\cdot}NH_4{\cdot}C_3H_5O_3{\cdot}2H_2O.$$

The salts also differ considerably in properties.

59. "*The Colouring Principles of Rubia sikkimensis.*" By A. G. Perkin and J. J. Hummel. (*Trans.*, 1893, 1157).

The authors have separated both purpurin and munjistin or purpuroxanthincarboxylic acid from this root; they point out that the results show that it is nearly identical as regards colouring principles with the closely allied *Rubia munjistin.*

60. *The Colouring and other Principles contained in Chay Root.*" By the same. (*Trans.*, 1893, 1160).

Chay root is the root of *Oldenlandia umbellata*, and is used as a dye-stuff in India; a large number of distinct products were isolated by extracting it either with an aqueous solution of sulphurous acid, or with lime-water, alcohol, and other solvents, viz., two substances of the formula $C_{16}H_{12}O_5$, both of which are shown to be anthragalloldimethyl ethers; a monomethyl ether of alizarin crystallising in orange needles melting at 178—179°; a resinous yellow substance, possibly an isomeric methyl ether, of alizarin in an impure form; metahydroxyanthraquinone; a yellow substance melting at 141°, which yields alizarin when heated with sulphuric acid; ruberythric acid; rubichloric acid; alizarin; a wax of the formula $(C_{10}H_{18}O)_2$, melting at 87—88°; and cane-sugar.

61. "*Phenylnaphthalenes. I. α-Phenylnaphthalene.*" By F. D. Chattaway, B.A. (*Trans.*. 1893, 1185).

It is shown that α-phenylnaphthalene can be synthesised in several ways, but that the yield in all cases is unsatisfactory. The best method is by the action of α-chloronaphthalene on benzene in the presence of anhydrous aluminium chloride. α Phenylnaphthalene is obtained as a thick, oily liquid, which solidifies on long standing, affording a fatty-looking mass without definite crystalline form. It boils at 324—325°, and is readily soluble in alcohol, ether, and benzene, but cannot be obtained crystalline from these solutions, being deposited on evaporating them in oily drops. It volatilises with steam, and possesses a peculiar odour resembling both naphthalene and diphenyl.

62. "*The Vapour Pressures, Molecular Volumes, and Critical Constants of Ten of the Lower Ethereal Salts of Acids of the Acetic Series.*" By Sydney Young, D.Sc., F.R.S., and G. L. Thomas, B.Sc. (*Trans.*, 1893, 1191).

The authors' chief object was to ascertain how far the generalisations of Van der Waals regarding "corresponding" temperatures, pressures, and volumes, are true for the members of a group of allied compounds. It has already been shown by one of them that the generalisations hold good, with a close approximation to accuracy, in the case of the four mono-haloid derivatives of benzene, but that when compounds of different chemical character are compared much greater deviations are to be observed, more especially as regards the absolute temperatures (boiling points) at corresponding pressures. It has also been shown that among the substances so far studied the deviations are greatest in the case of acetic acid and the alcohols, and it becomes therefore of additional interest to examine the behaviour of the salts formed by the interaction of the fatty acids and alcohols. The critical and other constants of a number of these have been determined by several observers, but the results are far from concordant, owing probably to imperfect purification of the substances examined. Two samples of each etherea salt were employed: one was prepared from the acid or anhydride and the alcohol; the other was obtained from Kahlbaum. All were carefully purified, and their purity was proved both by the constancy of their boiling-points and by the agreement between the boiling-points, relative densities, and critical temperatures and pressures of the two samples.

The investigation shows that, although the results obtained with the ten compounds are in fair agreement with the generalisation of Van der Waals,—in close agreement so far as the molecular volumes of liquid are concerned,—yet the deviations observed are related to their composition.

The ratios of the absolute temperatures to the absolute critical temperatures at any series of corresponding pressures are clearly dependent on the molecular weights, though this is apparently not the case with the ratios of the molecular volumes of either liquid or saturated vapour to the critical volumes.

The composition of the isomeric ethereal salts appears, however, to influence all the ratios, those for the formates being lowest when the absolute temperatures or volumes of saturated vapour are compared and highest in the case of the volumes of liquid. The ratios for the acetates, on the other hand, are highest in the case of the absolute temperatures and of the volumes of saturated vapour, and lowest for the volumes of liquid.

The presence of the iso-group in methylic isobutyrate appears to have a distinct influence on the ratios. The ratios of the actual critical densities to the theoretical densities (for a perfect gas) show a maximum variation of 2 per cent; the mean value, 3·91, is somewhat higher than that (3·76) for the majority of substances previously studied; it is, however, lower than for the alcohols and for acetic acid.

The ratios of the absolute temperatures and of the volumes of liquid and saturated vapour at corresponding pressures to the critical constants, also the values of PV/T at the critical points, are compared with those of the substances previously studied, and it is found that the ethereal salts form a separate group.

The twenty-two compounds for which data are available fall into four groups:—(1) The ethereal salts, (2) the alcohols — methyl alcohol being especially abnormal, (3) acetic acid, (4) ether, benzene and its haloid derivatives, carbon and tin tetrachlorides.

63. "*The Fermentation of Dextrose, Rhamnose, and Mannitol by a Lævolactic Ferment.*" By George Tate, Ph.D.

In studying the micro-organisms that attack ripe pears the author has had occasion to isolate an organism that under aërobic conditions brings about lævolactic fermentation of the hexoses, dextrose, mannose, and galactose, and also of mannitol, but an inactive lactic fermentation of the methylpentose rhamnose (isodulcite).

The products of the fermentation of dextrose, mannitol, and rhamnose have been quantitatively determined: nine molecules of dextrose are found to yield two molecules of alcohol, one of succinic acid, seven to eight of lævolactic acid, and smaller molecular proportions of formic and acetic acids.

Mannitol yields the same products, but in different proportions, there being a greater yield of alcohol and slightly greater yield of lævolactic acid.

Neither alcohol nor formic acid was found among the products of the fermentation of rhamnose; nine molecules of this sugar afforded approximately five molecules of acetic acid and four molecules of optically inactive lactic acid.

The action of the organism as a lævolactic ferment of dextrose was found to be unchanged after cultivating the parent cells in fluids containing rhamnose, inactive acid being formed.

The organism which is referred to as a lævolactic ferment from its action upon the typical sugar dextrose belongs to the class of ascobacteria, and can develope so as to produce two forms of growth, widely differing in macroscopic appearance — one in which rods and cocci predominate, a second in which the organism propagates as an ascobacterium.

64. "*Derivatives of Quinone containing Halogens. Part III. Derivatives of Quinhydrone.*" By Arthur R. Ling and Julian L. Baker. (*Trans.*, 1893, 1314).

Quinhydrone melts at 170—171°. The authors have obtained a compound having the composition of a *monochloroquinhydrone*, which melts at 145°, by gently heating a solution of quinone and monochloroquinol in chloroform; under somewhat similar circumstances Clark (*Amer. Chem. Journ.*, xiv., 574) obtained a small amount of quinhydrone. They have also obtained an isomeric compound melting at 132—133° by evaporating an ethereal or alcohol solution of quinol and monochloroquinone. When either of these isomerides is boiled with light petroleum they dissociate, and their constituents then interact, giving rise to dichloroquinhydrone, which is dissolved by the light petroleum, and quinhydrone, which remains undissolved.

*Dichloroquinhydrone*, $C_6H_3ClO_2,C_6H_3Cl(OH)_2$, is obtained by mixing solutions of monochloroquinone and monochloroquinol, and also by partially oxidising a solution of monochloroquinol with ferric chloride. It crystallises from water in dark violet needles containing one molecular proportion of water, melting at 70—72°; these are rendered anhydrous when kept over concentrated sulphuric acid, and then melt at 93—94°.

*Tetrachloroquinhydrone*,—

$$C_6H_2Cl_2O_2,C_6H_2Cl_2(OH)_2+2H_2O,$$

was described by Städeler in 1849. It is obtained in the form of dark violet needles by triturating paradichloroquinone and paradichloroquinol with water, and also by partially oxidising a solution of paradichloroquinol; the authors find that it melts between 105° and 140°, but has no definite melting-point. They confirm Städeler's observations that it loses its water of crystallisation when kept over concentrated sulphuric acid, becoming light yellow; the crystalline form of the anhydrous compound appears to be the same as that of the hydrated compound. An isomeride is obtained when metadichloroquinol and an excess of metadichloroquinone are boiled with a mixture of benzene and light petroleum; it separates from the filtrate in long, brown, prismatic needles, and melts at 135°.

*Hexachloroquinhydrone.*—A substance of the composition $C_{12}H_4Cl_6O_4+\frac{1}{2}H_2O$ is obtained by triturating trichloroquinone and trichloroquinol with water; it melts at 115—117°, and does not alter in weight when kept over concentrated sulphuric acid.

The authors failed to obtain octochloroquinhydrone, and conclude, from numerous experiments which are described, that this compound is non-existent.

*Dibromoquinhydrone*, $C_6H_3BrO_2,C_6H_3Br(OH)_2$, crystallises from water in anhydrous, dark, bronze-coloured needles, and melts at 98°.

*Tetrabromoquinhydrone* is obtained by boiling an aqueous solution of paradibromoquinol with an excess of paradibromoquinone; it separates, when the filtrate is rapidly cooled, in dark violet needles of the composition $C_6H_2Br_2O_2,C_6H_2Br_2(OH)_2+2H_2O$, and melts at 145—150°. It loses its water of crystallisation, and becomes light-coloured when kept over concentrated sulphuric acid.

*Dichlorodibromoquinhydrone*, prepared from paradichloroquinone and paradibromoquinol, crystallises from water in bluish-black needles containing two molecular proportions of water; it melts at 130—135°, and loses its water of crystallisation, becoming light yellow coloured when kept over concentrated sulphuric acid. An isomeride is obtained from paradibromoquinone and paradichloroquinol; it resembles the last-described compound and becomes pale brownish-yellow, losing its water of crystallisation when kept over concentrated sulphuric acid.

*Ordinary Meeting, November 2nd, 1893.*

Dr. Armstrong, President, in the Chair.

Messrs. Edmund Lamb, James A. Audley, Henry Bailey, and Charles Mills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Edmund Bowman, Ash Leigh, Bowdon, Cheshire; Henry Fielden Briggs, Roseneath, Torquay; Frank Browne, Government Civil Hospital, Hong Kong; John Dixon Brunton, Wire Mill, Musselburgh; Charles March Caines, 11, Clockhouse Road, Beckenham, Kent; Thomas Petson Carswell, 369, Scotswood Road, Newcastle-on-Tyne; Harry J. Chaney, 29, Chalcot Crescent, Regent's Park, London; Allan Thomas Cocking, 39, Lister Street, Rotherham; John A. Craw, 2, Millgate, Cupar Fife; Charles Sordes Ellis, 17, Bloomsbury Square, W.C.; Alexander M. Forrester, 22, Scotia Street, Glasgow; Henry Garnett, 2, Bartholomew Villas, Kentish Town, N.W.; William Hotton Grieve, 226, Friern Road, East Dulwich; Harry Edwin Hadley, The School of Science, Kidderminster; Henry Ormsby Hale, Oundle School, Northamptonshire; Harold Harris, Denmark House, Tuffley Avenue, Gloucester; William Hesketh, B.A., School House, Ferriscowles, Blackburn; Harold B. Holthouse, 42, St. Ann's Valley, Nottingham; Alexander Sinclair Hughson, 12, Myrtle Crescent, South Shields; Bertram Hunt, F.I.C., 5, Queen's Crescent, Glasgow; Richard Savory Ladell, 155, Praed Street, Hyde Park, London; William Fred Mawer, 16, Fentiman Road, S.W.; J. R. Morgan, Leydenburgh, Port Hall Street, Brighton; Frederick Morton, 101, Quarmby Road, Huddersfield; George F. Payne, M.D., Atlanta, Georgia, U.S.A.; Thomas Beilby Rawlins, 2, Levan Street, Pollokshields, Glasgow; George Percival Rees, Ely House, Basford, Stoke-on-Trent; Thomas Anderson Reid, Lostock Gralam, Northwich; Herbert Santer, Albion Brewery, Caledonian Road, N.; Philip Schidrowitz, 102, Oxford Gardens, Notting Hill, W.; W. Edgar Sims, B.Sc., Stafford House, Longsight, Manchester: Frederick Shapley, Whittier, Fuller, and Co., San Francisco; Frederick Spencer, Rose Villa, Uttoxeter, Staffs.; Robert Curling Styles, Knockhall, Greenhithe, Kent; Jocelyn Field Thorpe, Gloucester House, 20, Larkhall Rise, Clapham; William Herbert Walden, 55, Clapham Road, S.W.; Frank Ernest Welchman, 16, Carlton Road, Putney Hill, S.W.; William Gilchrist White, Lamb Roe, Whalley, Lancashire; Edward Humphreys Winder, 37, Vincent Square, S.W.; Stanley Wyndham, Ph.D., Judson, Florida, c/o Trenton Phosphor Co.

Of the following papers those marked * were read:—

*65. "*The Action of Bromine on Azobenzene.*" A correction. By Henry E. Armstrong.

It was pointed out by me in a recent note (*Proc. Chem. Soc.*, 1892, p. 194) that a compound represented by a formula such as is assigned to azobenzene, Ph·N:N·Ph, did not come within my "colour rule"; at the same time I drew attention to Werigo's *colourless* tetrabromazobenzene, and stated that Mr. Mills, at my request, had undertaken to further study the bromo-derivatives of azobenzene, and had already confirmed Werigo's observation.

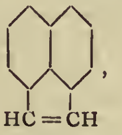
According to Werigo, tetrabromazobenzene melts at 320°; the product obtained by Mr. Mills charred at a high temperature without melting; when boiled with tin and muriatic acid, it gave a tetrabromobenzidine, which was readily purified by crystallisation from boiling xylene; this melted at 285° (uncorr.), and proved to be identical with that prepared from benzidine, following the directions of Claus and Risler. This benzidine derivative was converted into a tetrabromodiphenyl melting at 189° (uncorr.), from which a small quantity of dimetabromobenzoic acid was obtained by oxidation.

During the course of the experiments, Mr. Mills was gradually led to notice that the original product from azobenzene was very similar to tetrabromobenzidine, and he eventually satisfied himself by repeatedly crystallising it from xylene that it was, in fact, nothing but impure tetrabromobenzidine. The difference in composition between tetrabromazobenzene and tetrabromobenzidine is so small that it is practically impossible to decide by analysis which compound is under examination; and the fact that tetrabromobenzidine is destitute of basic properties renders its differentiation difficult. Werigo's tetrabromazobenzene must therefore be struck off the list of known compounds; and no argument as to the constitution of azobenzene can be based on its behaviour with bromine.

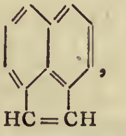
*66. "*The Origin of Colour.* (X.) *Coloured Hydrocarbons.*" By Henry E. Armstrong.

Graebe, in a recent note (*Ber.*, 1893, 2354), adduces what appears to be satisfactory evidence that the acenaphthylene, $C_{12}H_8$, discovered by Behr and Van Dorp, is actually a *yellow* hydrocarbon, and contends that the colour of this hydrocarbon and also that of the red hydrocarbon from fluorene (*cf. Proc. Chem. Soc.*, 1892, 192) is to be regarded as, in the first instance, conditioned by the presence of the group $>C:C<$. He ascribes the non-appearance of colour in ethylene derivatives generally to a secondary influence exercised by the groups displacing the hydrogen atoms in ethylene.

The problem is of such importance that I will venture to point out that in the case of coloured substances generally, the type of the series is itself always coloured —the only exception which I can call to mind being iodoform (*cf. Proc. Chem. Soc.*, 1893, 62). Acenaphthylene, no doubt, cannot well be represented otherwise than by the formula—



but if possessed of an *ethenoid* structure akin to that of anthracene, an "explanation" of its colour may be given similar to that which I have put forward in the case of anthracene and of certain coloured quinoline derivatives (*Proc. Chem. Soc.*, 1893, 63). On inspecting the formula—



it will be seen that the carbon atoms of the one nucleus are attached to the benzene nucleus on the left in ortho-positions and by ethenoid linkages; in other words, the hydrocarbon is an orthoquinonoid derivative. The external coupling is, in a measure, comparable with that which occurs in compounds such as methylene blue, &c., and it is this circumstance, perhaps, which causes the colour of the hydrocarbon to be so much more intense than that of anthracene, for example.

(To be continued).

## PHYSICAL SOCIETY.

*Ordinary Meeting, November 10th, 1893.*

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Mr. R. S. Cole was elected a Member of the Society.

A paper on the "*Separation of Three Liquids by Fractional Distillation*," by Prof. F. R. Barrell, M.A., B.Sc., G. L. Thomas, B.Sc., and Prof. Sydney Young, D.Sc., F.R.S., was read by Prof. Young. Accepting the results obtained by F. D. Brown in his experiments on the variation in the composition of the distillate from a mixture of two liquids, viz., that the relative quantities of the two substances in the vapour at any instant are proportional to the weights of the substances in the still, multiplied by the ratio of their vapour pressures, the authors write Brown's equation in the form—

$$\frac{d\xi}{d\eta} = c\,\frac{\xi}{\eta}$$

where $\xi$ and $\eta$ are the weights of the two liquids in the still and $c$ the ratio of their vapour pressures. Taking $c$ as constant, the above equation is integrated, and from the resulting expressions curves are plotted showing the changes in composition that take place during the distillation. Assuming that a similar law holds for three liquids, A, B, and C, viz.—

$$\frac{1}{a}\,\frac{d\xi}{\xi} = \frac{1}{b}\,\frac{d\eta}{\eta} = \frac{1}{c}\,\frac{d\zeta}{\zeta}$$

the composition of the distillate at any instant is calculated.

Taking $a=4$, $b=2$, and $c=1$ (numbers nearly proportional to the vapour pressures of methyl, ethyl, and propyl acetates) numerous curves are plotted showing the progress of the separation at various stages of fractionation. These curves show distinctly that, although fractions containing large proportions of the liquids A and C, of lowest and highest boiling-points respectively, can be easily separated, the middle substance, B, is much more difficult to obtain in a state of purity. Consideration of these curves led the authors to see that by carrying out the fractionation in a particular way it was possible to separate the mixture into two portions, one containing only A and B, and the other B and C. These mixtures of two liquids would then be fractionated in the usual manner. This process was carried out on a mixture of methyl, ethyl, and propyl acetates, the results of which are given in considerable detail in the paper. The remarkable agreement between the densities of the ethyl acetates obtained respectively from the mixtures (A+B) and (B+C), as well as the fact that the densities of the separated liquids were the same as before the mixing, shows conclusively that the method employed was highly successful.

Prof. Ramsay said the paper was a most valuable one, and would be a great aid to chemists. Distillations were usually carried out by "the rule of thumb," with the result that absolutely pure liquids could rarely be obtained.

The President enquired whether the curves representing the progress of distillation could be constructed from the very complete experiments made, and so test the assumed law.

Prof. Young thought this not possible from the numbers obtained. To test the law in this way would be very laborious.

A "*Note on the Generalisations of Van der Waals regarding 'Corresponding' Temperatures, Pressures, and Volumes*" was read by Prof. S. Young. In November, 1891, the author read a paper on the same subject (*Phil. Mag.*, Feb., 1892), and gave the critical molecular volumes of some twelve substances as calculated by M. Mathias. Since then a few small errors have been found in the calculation, and the author's corrected values are now given. The vapour pressures, molecular volumes, and critical constants of ten esters (methyl formate, acetate, propionate, butyrate, and isobutyrate; ethyl formate, acetate, and propionate; and propyl formate and acetate) have recently been determined (*Trans. Chem. Soc.*, lxiii., p. 1191). In the present paper the absolute temperature and volume of the twelve substances are given in terms of their critical constants, and tables given showing respectively the ratio of boiling-points (abs. temps.) at corresponding pressures, to absolute critical temperatures; the ratios of volume of liquid at corresponding pressures to the critical volume; and ratios of volume of saturated vapour at corresponding pressures to critical volume; for the halogen derivatives of benzene, carbon tetrachloride, stannic chloride, ether; methyl, ethyl, and propyl alcohols; and acetic acid; and the extreme values for the ten esters previously mentioned. Whilst showing fair agreement with each other, the differences between them exceed errors of experiment. The ratios also indicate that the substances can be arranged in four groups, thus tending to show that molecular weight and chemical constitution have some influence on the results. The differences found would probably result from the presence of complex molecules such as are known to exist in acetic acid.

If Van der Waals's generalisations were strictly true, the ratio $\frac{PV}{T}$ at the critical point should be constant for all substances, as also the ratio $\frac{D}{D'}$, of the actual to the theoretical density (for a perfect gas) at the critical point. On comparing these quantities only a rough approximation is found, but the grouping of the compounds is again well marked.

Prof. Ramsay was not sure that the existence of complexes would alter the molecular volume in the liquid state; for liquids seem very compact. Experiments on the surface energy of liquids had proved that complex molecules do exist in the alcohols and acetic acid. Dr. Young's conclusion was, therefore, confirmed by experiments of an entirely different nature.

Prof. Herschel was gratified to see Van der Waals's theory so well borne out in liquids, and hoped to see it extended to solids. The recent researches of Prof. Roberts-Austen on alloys seemed to point in this direction.

Mr. Rogers said molecular complexes do exert an influence on the properties of substances, as had been shown by Prof. Thorpe's viscosity experiments. Van der Waals's generalisations should therefore be looked at from a chemical as well as a physical point of view.

The President thought the numbers brought forward showed fair agreement, especially when it was remembered that Van der Waals took no account of the complex molecules. Contrary to Prof. Ramsay, he would rather expect aggregation to affect the molecular volumes in the liquid state, for only about one-fifth the space was supposed to be occupied by matter. On the other hand, the relatively small contraction of liquids on cooling did not support this view.

"*An Instrument for Drawing Conic Sections*" was exhibited and described by Mr. J. Gillett, B.A.

This consists of a spindle inclined to a plane board, and a tube fixed to the spindle at an angle. A pencil which passes through the tube traces out a cone in space as the spindle is turned, and on sliding the pencil through the tube so as to keep its point against the plane, the point traces out a conic—the section of the cone made by the plane of the board. A circle, ellipse, parabole, or hyperbole can be drawn according to the inclination of the spindle to the board.

Prof. Henrici said a similar instrument had been described in an Arabian manuscript 1000 years old, and had been independently re-invented by both a German and an Italian mathematician. He thought the fact of angle between the spindle and the tube in Mr. Gillett's instrument not being adjustable, was a disadvantage.

Mr. Inwards and Prof. Herschel also took part in the discussion, to which Mr. Gillett replied.

Zero-point in Measuring Pipettes.—Ch. O. Curtman (*Pharm. Rundschau*).—The author places the zero-point at the meniscus of the last drop retained by capillary attraction.

## CORRESPONDENCE.

### PREPARATION OF HYDROGEN.

*To the Editor of the Chemical News.*

Sir,—With regard to Mr. Ball's recent discovery (Chem. News, vol. lxviii., p. 284) I beg to refer him to the new German edition of Graham Otto's "Compendium," vol. i., p. 99, published as early as 1878, where he will find the following note:—

"More powerfully still (than the metal) acts one drop of platinum chloride. . . . An action similar to platinum have solutions of gold, copper, silver, zinc, antimony, bismuth, and lead, and it is said that an addition of the chloride of either cobalt or nickel still surpasses the action of platinum."—I am, &c.,

H. Kemp.

St. Xavier's College, Bombay,
October 28, 1893.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 18, October 30, 1893.

**The Yield of the Vine in the Season 1893.**—M. Chambrelent.—The vintage this autumn in the Gironde and the Camargne has been unusually early and exceptionally good both in quantity and quality.

**Carboxylated Derivatives of Dimethylaniline (Dimethylamidobenzoic Acids).**—Charles Lauth.—The introduction of the group $CO.OH$ in dimethylaniline in substitution for an atom of hydrogen, and the position which it occupies with reference to the amidogen in the molecule, gives to each of the isomers obtained peculiar properties, especially as regards the production of colouring substances. When the position occupied is ortho we obtain carboxylic colouring substances soluble in alkalis and capable of dyeing with metallic mordants. If it is para we obtain colouring-matters not carboxylic, and identical with those of dimethylaniline itself. When the position is meta the aptitude to form tinctorial substances has almost entirely disappeared.

**Temperature of Baking Bread.**—Aimé Girard.—Referring to M. Balland's paper (*Comptes Rendus*, October 16, 1893), the author states that the temperature in the middle of the dough is 101°, not in *some*, but in all cases.

No. 19, November 6, 1893.

**A New Method of Preparing Methylamine, and on the Constitution of Hexamethylene-tetramine.**—MM. Trillat and Fayollal.—If we reduce by means of zinc and hydrochloric acid the aqueous solution of the ammoniacal compound of formaldehyd, and heat the product in presence of soda, there is evolved a strong odour of methylamine. 100 grms. of formic aldehyd at 33 per cent are mixed in the cold with an aqueous solution of ammonia until no more heat is evolved. We then add at once 200 grms. zinc powder, and there is then allowed to flow gently into the mixture 750 grms. ordinary hydrochloric acid. This addition is made in the cold, and should be effected in the space of from eight to ten hours. To the liquid there is added a large excess of sodium carbonate, and it is distilled by a current of steam. The distillate is received in dilute hydrochloric acid. Ammonia passes over first, and then methylamine. We obtain thus a mixture of the two hydrochlorates, which are evaporated, dried, and separated by absolute alcohol in heat. It may be considered as para.

**Alkaline Methyltartrates and Ethyltartrates.**—J. Fayollal.—The author describes the preparation of the lithium, sodium, potassium, and ammonium methyltartrates, and of the lithium, sodium, potassium, barium, and calcium ethyltartrates. He subjoins their specific rotatory powers in the form of a table.

**Researches on the Homologues of Gallanilide. Preparation of Galloparatoluide.**—P. Cazeneuve.—The author conjectured that as gallanilide, the anilide of gallic acid, is obtained by the action of aniline upon tannin, homologues of gallanilide might be obtained by analogous methods. Experience showed that only paratoluidine behaves like aniline, forming galloparatoluide.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 4.

**The Annular Vernier Burette.**—C. Meinecke (*Chem. Zeitung*).—This is a burette which permits of very accurate readings by means of a very fine auxiliary burette. The graduation is carried round the entire circuit of the burettes. The experimentalist titrates as usual, and if the liquid does not exactly stand at a degree it is allowed to flow into the vernier burette as far as the next degree, by which means it is possible to read to hundredths of a c.c.

**Weight Burette.**—M. Ripper (*Chemiker Zeitung*).—The liquid consumed is determined, not by volume, but by weight. This principle, first proposed by Hager and F. H. Morgan, is especially recommended in case of rather concentrated solutions. The equivalent is contained, not in 1 litre, but in 1 kilo. Ripper's apparatus is a shortened and proportionately expanded glass cock burette, which can be suspended to the balance by means of a wire, or clamped by its neck and its lower end to a stand. The author enumerates the following advantages of weighing as compared with measuring:—1. Independence of the temperature of the standard solutions. 2. Independence of correct graduation. 3. No errors in reading off. 4. No errors from the adhesion of the standard solutions to the sides of the tubes. 5. Equal degree of accuracy on using different quantities of liquid.

**Sublimation of Iodine, Benzoic Acid, &c.**—J. Hertkorn (*Chemiker Zeitung*).—The author uses, to contain the substance to be sublimed, a flat capsule of enamelled iron provided with a channel-shaped margin, into which fits a cone of enamelled iron closed with a doubly perforated cork. The channel is filled with mercury, oil, melted paraffin, &c. The stopper closing the upper orifice of the cone has two apertures. Through one of these there passes an escape tube, which can be closed by means of a caoutchouc pipe and a pinch-cock. Through the other perforation passes a long pear-shaped refrigerator extending into the cone.

**Apparatus for the Fractionated Distillation of Liquids.**—M. Ekeberg (*Chemiker Zeitung*).—This arrangement is adapted for the distillation of liquids boiling between 100° and 250°. The pipe for conveying away the vapours is coiled spirally and passes through an air-bath, the temperature of which can be kept constant to 0·2° by means of an electric thermo-regulator.

**Safety Arrangement Against Explosions.**—P. Altmann (*Chemiker Zeitung*).—The object is to prevent the danger of explosions from the sudden extinction of gas-flames left without supervision. A ring composed of two metals having different coefficients of expansion is applied to the burner in such a manner that the one end is close to the flame, and is heated accordingly. The ring is thus expanded, and a lever fixed at its other end slides over the arm of a cock which it carries along when the ring cools and contracts, and thus turns off the gas.

**Photography as a Substitute for Direct Observation in Polarising.**—Chauvin and Charles Fabre.—*Comptes Rendus*, cxiii., p. 691.

**Table for Calculating the Proportion of Phosphoric Acid from the Weight of Magnesium Pyrophosphate.**—Fr. Scheiding (*Chemiker Zeitung*).—The author assumes that if 0·5 grm. of the substance is taken, direct percentages of phosphoric anhydride are obtained. The table is not inserted.

**Arrangement for Determining the Quantity of a Volatile Ingredient Present in any Substance.**—O. Pettersson (*Chemiker Zeitung*).—Already inserted.

**Proposal for the Composition of Normal Weights for Analytical and Physical Weighings.**—A. Gawalowski (*Oel und Fett-Industrie*).—The author has found the subjoined alloy very suitable for the production of weights to resist gases, moist air, &c:—Aluminium, 80·0; fine gold, 8·0; fine silver, 2·5; platinum, 4·0.

**Proposals for Standardising in Acidimetry and Alkalimetry.**—E. Brentel (*Oest. Chem. Gesellschaft* and *Zeit. Anorganische Chemie*).—Already inserted.

**Comparisons of Various Methods for Standardising Normal Acids and Normal Alkalies.**—C. L. Parsons.—From the *Journal of Analytical Chemistry*.

**Standardising Normal Acids, especially for the Kjeldahl's Nitrogen Process.**—F. C. Wells.—From the *Journal of Analytical Chemistry*.

**Testing Burettes and other Measuring Vessels.**—H. L. Payne.—From the *Journal of Analytical Chemistry*.

**Burettes with Automatic Adjustment for the Zero-point.**—H. R. Procter (*Chemiker Zeitung*) and St. Krawczynski (*Berichte*).—Procter's instrument is quite similar to that formerly proposed by J. Stumpf (*Zeit. Anal. Chemie*, 29, 590).

**Pipettes for Poisonous Liquids.**—Al. F. Reid.—From the Chemical News.

**A Cock-pipette.**—Carl Meissner (*Chemiker Zeitung*).—This instrument requires the accompanying figure.

## NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Decomposition of Salt by Electrolysis.**—Can any reader inform me where I shall find the latest results that have been obtained on the practical scale in the decomposition of salt by electrolysis?—J. W.

## MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.

Wednesday, 29th.—Society of Arts, 8. "The Regulation of Street Advertising," by Richardson Evans.

THE CHEMICAL NEWS.

Vol. LXVIII., No. 1775.

## VEGETATION IN AN ATMOSPHERE DEVOID OF OXYGEN, AND CONSIDERATIONS ON THE DAWN OF ANIMAL LIFE.

By Dr. T. L. PHIPSON, F.C.S.,
Graduate of the Faculties of Science and Medicine of the University of Brussels, Member of the Chemical Society of Paris, &c.

In various papers published in the Chemical News during the present year, I have endeavoured to show that in the earliest ages of the earth, when life first made its appearance, plants (*anærobies*) must have been formed before animals (*aërobies*), as the presence of unoxidised substances in the primitive rocks prove that free oxygen was absent from the primitive atmosphere. The experiment on vegetation in hydrogen, which I published not long since (Chem. News, vol. lxvii., p. 303), shows that free hydrogen could not have existed in the primitive atmosphere any more than it can exist for any length of time in the atmospheric air of our days without becoming water.

On account of its feeble affinities, nitrogen alone could have formed the atmosphere in the earliest ages of our planet's history; and, previous to the advent of life, this primitive atmosphere was charged with carbonic acid and vapour by volcanic action, such as we see manifested to a considerable extent at the present time

Hence the earlier vegetation of the globe developed in an atmosphere devoid of free oxygen, consisting of nitrogen, carbonic acid, and vapour, and *the whole of the oxygen now present in the earth's atmosphere is due to vegetation* extending over immense periods of time.

As the ancient plants were evidently anærobic, it was interesting to ascertain whether the plants of the present time were essentially of the same nature, and my experiments have shown me that they are; also that they must have preceded animal life—the latter resulting from the gradual transformation of anærobic cells into aërobic cells, *as a consequence of the changing conditions;* that is, the oxygen constantly poured into the air by vegetation.

At what precise geological period oxygen became present in sufficient quantity to allow of animal life might appear an interesting problem for the geologist, but *no such period will ever be determined*, because the change must have been very gradual; and the study of the lower forms of vegetable and animal life show us that there is no hard and fast line between the two kingdoms. There is no such thing to be discovered as "the first vestiges of animal life." As the oxygen evolved from the anærobic cells became gradually a greater factor in the composition of the air, these cells had to accustom themselves to it, until some became aërobic, and by their vital functions actually supplied carbonic acid to the air instead of oxygen.

In addition to the experimental notes I have already published to demonstrate the truth of these considerations, I may call attention to one experiment made with *Convolvulus arvensis* (a plant I have often used for this purpose) vegetating in an atmosphere devoid of free oxygen; whilst two other plants of the same species were growing alongside the apparatus in ordinary atmospheric air. It will be seen that the plants of the present day are anærobic, like those of the older periods, and that free oxygen in the air is not essential for their existence.

This experiment with *C. arvensis* vegetating in what may be termed a "primitive atmosphere," is typical of what occurs with all the phanerogamic plants mentioned in my previous papers, and with all the green *Algæ*, such as *Protococcus pluvialis* and the minute *Microcystis*, or "green matter of Priestley," that develops in spring water exposed for some weeks to the light.

The nitrogen in my former experiments was obtained from pure sulphate of ammonia, but more recently I have got it by the action of potash and pyrogallol on atmospheric air. It will be seen, however, by what follows, that *the same volume of nitrogen may be used over and over again* as it undergoes no alteration in volume or properties except those due to the oscillations of temperature and pressure. The apparatus consists simply of a graduated tube, wide enough to admit the plant easily, standing over water containing minute quantities of all the substances known (or supposed) to be useful to vegetation, and kept supplied with carbonic acid. Alongside of the graduated tube stands another smaller tube full of water; into this carbonic acid is introduced, at first, once a day; it displaces the water, but in the course of twenty-four hours or so, the water has absorbed this gas, and the tube is again full of water. Carbonic acid is again passed into it the next day, and the water displaced, saturated with carbonic acid, thus finds its way to the roots of the plant. In this manner the water of the basin in which stand the two tubes is kept supplied with a good quantity of carbonic acid. The whole is exposed to a constant northern light, such as is used by artists, which I have found preferable to a southern aspect or to the direct rays of the sun; the temperature of the room has varied from 15° to 32° C. One-half of the water in the little basin is covered to procure darkness for the roots, and a certain quantity of carbonic acid is also let into the graduated tube from time to time.

In this primitive atmosphere of nitrogen, carbonic acid, and watery vapour, vegetation is tolerably prosperous in spite of the confined condition of the air. The carbonic acid is absorbed and replaced by free oxygen, so that after a certain lapse of time the gas in the graduated tube approaches the composition of atmospheric air, and *can even be made richer than the latter in oxygen.* I have already shown that in pure carbonic acid a plant does not prosper long, but with a basis of nitrogen and vapour of water it will prosper with a large amount of carbonic acid for a considerable time, and will transform this carbonic acid into oxygen, volume for volume, until there is more oxygen in the gas than in common air.

First, 75 c.c. of pure nitrogen (reduced to 0° C. and 30 inches barometer) is introduced, and the plant being put in makes the whole 102 c.c. Then, a certain amount of carbonic acid is let in, and the volume of gas oscillates during the experiment from 102 to 127 or 130 c.c., according to the temperature and pressure, and the quantity of carbonic acid above the water at the time of observation.

The little plant was introduced on July 25, its height being then 30 divisions of the tube. On the 26th it had grown to 37 divisions; on the 28th, to 44 divisions; on the 29th, to 48; and on the 30th, to 51 divisions, when it began to curve. On July 31 it had formed a new leaf and was curving, occupying 52 divisions. On August 1 it had curved considerably, as all plants of the *Convolvulus* genus do, and measured only 50 divisions in height; but on the second it had shot up again to 64 divisions. It appeared very healthy. On August 3 it attained to 68 divisions. On the 5th there were new leaves formed, and the plant measured 70 divisions. During August 6, 7, 8, and 9, the plant was healthy and two more leaves had formed. The water being well supplied with carbonic acid, and a little introduced into the graduated tube, I left the experiment till September 18. On September 18 it had grown to 90 divisions, and by the 30th of the month to 94—nearly to the top of the graduated tube.

On October 2 it began to turn yellow, as did the two plants of the same species growing in the water outside the apparatus, as "witnesses." They all put on their autumnal tints at the same time, and were all dead by October 30.

The gas in the graduated tube (reduced to 0° C. and 30 inches barometer) measured 95 c.c. It was analysed on the 30th, and gave exactly—

|  |  |
|---|---|
| Nitrogen .. .. .. | 75 |
| Carbonic acid .. .. | none |
| Oxygen .. .. .. | 20 |
| Total .. .. .. | 95 c.c. |

In the course of three months and seven days, or ninety-eight days, the plant had grown from 30 to 94 divisions, not counting the curve natural to the *Convolvulus*, and had converted all the carbonic acid into oxygen, leaving the nitrogen exactly as it was at the commencement of the experiment. At the end of these fourteen weeks, the atmosphere of the graduated tube was thus found to be *richer in oxygen than ordinary atmospheric air*, which shows what would happen to the earth's atmosphere if there were an excessive supply of carbonic acid and vegetation did not deteriorate: *the oxygen of the air, due to plant life alone, would increase year by year*.

In the present state of things there is a kind of equilibrium *apparent* (not real), as during the last fifty or sixty years no excess of oxygen has been detected by analysis of the air. But what are fifty or sixty years compared to the thousands of centuries by which Nature counts her periods?

Hotham Villa, Putney,
Nov. 14, 1893.

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ON THE

## TEACHING OF INORGANIC CHEMISTRY.

By MARGARET D. DOUGAL.

(Concluded from p. 248).

Although vanadium is very nearly related to phosphorus as regards its compounds, there is, nevertheless, much to be said against the above grouping, particularly when we consider the corresponding members of Family VI. Even if it were possible to separate phosphorus from arsenic in order to place it in association with vanadium, nobody would separate selenium from sulphur in order to place the latter in association with chromium. It is therefore obvious that we are not able to use the above arrangement. A somewhat nearer consideration at once makes evident the reason for this apparent difficulty.

Titanium and zirconium are not quite analogous to silicon. On the curve of atomic volume they stand on the descending line, whilst the two first members — carbon and silicon, together with boron and aluminium—are represented on the lowest point of the curve. Still greater is the difference between phosphorus and vanadium, for the former is on the ascending line, and is accordingly easily fusible and volatile, and the latter is on the descending line as a very difficultly fusible element. We have, therefore, along with nitrogen and phosphorus, the volatile, easily fusible elements arsenic, antimony, and bismuth to combine in one family, and to treat in like manner the two following families. Accordingly, from Family V., the main groups, consisting of four or five members, are formed of the easily fusible and readily reducible, and the sub-groups of the more infusible and difficultly reducible elements:—

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| N = 14·01 |  | O = 15·96 |  | F = 19·06 |  |
| P = 30·96 |  | S = 31·98 |  | Cl = 35·37 |  |
|  | V = 51·1 |  | Cr = 52·0 |  | Mn = 54·8 |
| As = 74·9 |  | Se = 78·87 |  | Br = 79·76 |  |
|  | Nb = 93·7 |  | Mo = 95·9 |  | — |
| Sb = 119·6 |  | Te = 125·0 |  | I = 126·54 |  |
|  | Ta = 182·0 |  | W = 183·6 |  | — |
| Bi = 208·9 |  | — |  | — |  |
|  | — |  | U = 238·8 |  | — |

In the description of these groups attention is drawn to the peculiarity that the chemical value, with respect to positive and negative elements, is now different, namely:

|  | In IV. | In V. | In VI. | In VII. |
|---|---|---|---|---|
| Towards positive .. .. | 4 | 3 | 2 | 1 |
| ,, negative .. .. | 4 | 5 | 6 | 7 |

In consequence of the negative character of these elements, their affinity to other negative elements is so feeble that they frequently are unable to hold in stable union the number of negative atoms, *e.g.*, of chlorine, corresponding to their chemical value. For instance, of the members of Family V., only P, Nb, Sb, and Ta form normal chlorides of the formula $RCl_5$, whilst $NCl_3$, $VCl_4$, and $BiCl_3$ cannot take up a further quantity of chlorine. Still more striking is this in Family VI., where only one normal chloride, $WCl_6$, is known, and even this readily parts with chlorine; and in VII., where, up to the present, no chloride, $RCl_7$, has been prepared. In order to allow the student more thoroughly to understand these intricate relations, the lower chlorides are somewhat more fully discussed:—

$$SbCl_5 \qquad TeCl_4 \qquad ICl_3$$
$$SbCl_3 \qquad TeCl_2 \qquad ICl$$

The degree of detail in which the individual members are treated depends on their relative importance.

The oxides and hydrates offer fewer irregularities; nevertheless, their composition is more difficult to grasp than those occurring in the first four Families.

The hydroxyl compounds are regarded as anhydro-acids:—

| IV. | V. | VI. | VII. |
|---|---|---|---|
| $RO_4H_4$ | $(RO_5H_5)$ | $(RO_6H_6)$ | $(RO_7H_7)$ |
| $RO_3H_2$ | $RO_4H_3$ | $(RO_5H_4)$ | $RO_6H_5$ |
| $RO_2$ | $RO_3H$ | $RO_4H_2$ | $RO_5H_3$ |
|  |  | $RO_3$ | $RO_4H$ |

The poly-acids are represented in an analogous manner:—

|  |  |  |  |
|---|---|---|---|
| $R_2O_7H_6$ | $R_2O_7H_4$ | $R_2O_7H_2$ | $R_2O_7$ |
| $R_2O_6H_4$ | $R_2O_6H_2$ | $R_2O_6$ |  |
| $R_2O_5H_2$ | $R_2O_5$ |  |  |

The composition of the acids poorer in oxygen is easily made clear in a similar way:—

$$PO_3H_3 \qquad SO_3H_2 \qquad ClO_3H$$

These regular formulæ are certainly more comprehensive than the representations in many text-books, as, for example, the representation of the different perchloric acids by the formulæ—

$$HClO_4+2H_2O \qquad HClO_5+H_2O \qquad HClO_4,$$

instead of by the typical formulæ corresponding to their behaviour—

$$H_5ClO_6 \qquad H_3ClO_5 \qquad HClO_4.$$

But the periodic acids and their silver salts of the regular composition—

$$H_5IO_6 \qquad H_3Ag_2IO_6 \qquad Ag_5IO_6$$

are regarded as molecular additions of silver oxide and water to $AgIO_4$ or $HIO_4$, although their behaviour in no sense agrees with such a representation.

Dr. Meyer again takes up the consideration of the elements in detail. In Family V., as nitrogen and its compounds differ so very much in their properties from the following substances, it is advisable to speak of this element once more. After the explosive halogen compounds have been mentioned, of the oxygen compounds, nitric acid and the nitrates are fully described; and from their products of decomposition the lower oxides follow. The other elements of the group are then dealt with: their occurrence, modes of extraction and properties, their halogen compounds, their oxides, hydrates, oxychlorides, sulphides, &c., chiefly in the same order as hitherto adopted.

Of Family VII. oxygen is the first member. As it has already been fully discussed, it only remains to deal with ozone. The chloroxides could be, indeed, regarded as chlorides of oxygen were it convenient to do so.

The following elements—sulphur, selenium, and tellurium—are spoken of together, as well as their compounds, with special mention of sulphur. The halogen compounds afford a striking example of the change in affinity strength with atomic weight, inasmuch as their stability increases from those of sulphur over selenium to tellurium. The consideration of oxygen compounds begins conveniently with sulphur dioxide, which leads up to the description of the manufacture of sulphuric acid. The sulphates are again—as the carbonates, nitrates, &c.—arranged in isomorphous groups.

The elements of Family VII. — fluorine, chlorine, bromine, and iodine—have, in connection with their preparation from their hydrogen compounds, been somewhat fully described, so that little now remains to be added. The compounds they form by their mutual union are likewise soon dismissed, but it is again indicated that in the cases of elements of very similar properties the mutual affinity appears to be weakened, so that the number of the halogen atoms frequently remains below the particular number denoted by the chemical value. The consideration of the oxygen compounds of the salt-formers conveniently begins with the lowest oxides and hydrates, inasmuch as these form the starting-point for the preparation of the higher oxides. That the latter correspond to the heptad elements of the type has already been mentioned.

The main groups of Family VII. having been discussed, there remain only the sub-groups. Formerly Dr. Meyer treated them in the same order as the main groups; latterly, however, he has adopted what he believes to be a better arrangement based upon the nature of the elements.

After Family V. the easily reducible elements have been dealt with as the main groups of the families, whereas in the first four families they constituted the sub-groups; so between IV. and V., as already mentioned, there is a discontinuity, which is obvious from the following classification :—

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| IV. | Main group .. | C, | Si, | Ti, | | Zr, | | — | | Th, |
| | Sub-group .. | | | | Ge, | | Sn, | | Pb, | |
| V. | Main group .. | N, | P, | | As, | | Sb, | | Bi, | |
| | Sub-group .. | | | V, | | Nb, | | Ta, | | — |

Accordingly, it is advisable to begin the consideration of the sub-groups with those of Family V., and to conclude with those of IV. We thus obtain the following series :—

| V. | VI. | VII. | VIII. | | | I. | II. | III. | IV. |
|---|---|---|---|---|---|---|---|---|---|
| V, | Cr, | Mn, | Fe, | Co, | Ni, | Cu, | Zn, | Ga, | Ge. |
| Nb, | Mo, | — | Ru, | Rh, | Pd, | Ag, | Cd, | In, | Sn. |
| Ta, | W, | — | Os, | Ir, | Pt, | Au, | Hg, | Tl, | Pb. |

This arrangement allows of the oxy-acids of the phosphorus, sulphur, and chlorine groups to be connected up with the isomorphous acids of vanadium, chromium, manganese, and their related acids, whilst the lower oxides of these groups form the natural link with those of the iron group, whose compounds rich in oxygen are generally very unstable.

The elements and compounds of these three sub-groups, V., VI., and VII., are then described and discussed; chromium and manganese, owing to their importance, being dwelt upon at greater length than the others.

The metals which are usually classed together as Family VIII., namely, the difficultly fusible heavy elements, Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt, are conveniently described in two divisions; first, Fe, Co, and Ni; and then the platinum metals. There remain, in conclusion, still a dozen somewhat easily fusible heavy metals, the description of which is much simplified when similar ones are compared together. The treatment of their compounds is rendered easy by reference to the main groups of the same families to which they are analogous. We have, for example, for the normal chlorides the series :—

| | | | |
|---|---|---|---|
| $CuCl$ | $ZnCl_2$ | $GaCl_3$ | $GeCl_4$ |
| $AgCl$ | $CdCl_2$ | $InCl_3$ | $SnCl_4$ |
| $AuCl$ | $HgCl_2$ | $TlCl_3$ | $(PbCl_4)$ |

Naturally, the variations from these types as shown by $CuCl_2$ and $AuCl_3$ are clearly pointed out. At the same time the weakness of the affinities is indicated by the fact that $TlCl_3$ is readily split up into $TlCl$ and $Cl_2$, whilst $PbCl_4$[*] cannot exist, at least, in an isolated condition.

Such is Professor Lothar Meyer's mode of presentation of the subject-matter of Inorganic Chemistry. He gives it as not the only one possible, and it is doubtless capable of modification in certain particulars; nevertheless it must be obvious that it is the outcome of much thought and experience, and as such, is well worthy of the attention and careful study of all who are concerned in the Teaching of Inorganic Chemistry.

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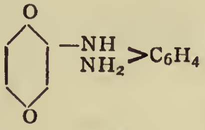
### THE

# INTERACTION OF QUINONES AND ORTHONITRANILINE AND NITROPARATOLUIDINE.[†]

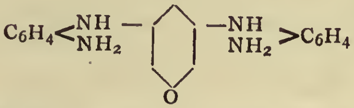
By Dr. JAMES LEICESTER, Ph.D., F.C.S.,
Lecturer on Chemistry and Metallurgy at the Merchant Venturers' Technical School, Bristol.

It is known that quinone and aniline interact, forming quinone-anilide, and the constitution of these compounds appears to be established.

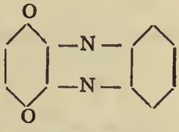
It was to be supposed that by an analogous interaction of orthodiamines and quinones substances would be obtained such as are represented by the following formula—



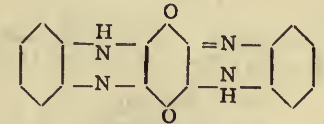
Or,



Or that action might proceed so far that quinone-phenazines or even quinone-fluorindine would result—



Quinone-phenazine.



Quininehomofluorindine.

Actually the interaction of orthophenylene diamine and quinone is found to give rise to a mixture of substances which are exceedingly difficult to isolate; therefore, in order to fully determine the nature of the action, a series of experiments have been carried out with orthonitrobases and quinones.

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[*] Lead tetrachloride, $PbCl_4$, has been recently isolated by H. Friedrich as a translucent, yellow, highly refractive liquid, readily decomposable into lead dichloride and chlorine. The much more stable lead tetracetate, $Pb(C_2H_3O_2)_4$, has lately been obtained by Hutchinson and Pollard. A corresponding propionate is also known.

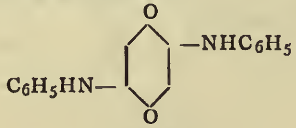
[†] *Ber. d. Deutsch. Chem. Gesell.*, xxiii., 2793: *Chem. Soc. Journ.*, Abstr., 1890, 1445.

### *Quinone-orthodinitranilide.*

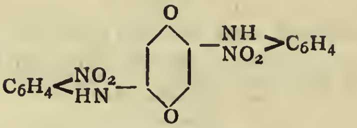
A solution in glacial acetic acid of three parts of quinone with 2·5 parts of orthonitraniline was heated for about two hours, the liquid being allowed to boil gently. On cooling the solution red crystals deposited, which were filtered off, and having been washed with a little glacial acetic acid and then with alcohol and ether were re-crystallised from hot absolute alcohol; thus obtained the products consisted of long red needles, melting at 305° C., with decomposition. On analysis it gave the following results:—

| | Found. | Theory, $C_{18}H_{12}N_4O_6$. |
|---|---|---|
| C .. .. | 57·3 p.c. | 56·8 p.c. |
| H .. .. | 3·1 „ | 3·1 „ |
| N .. .. | 14·8 „ | 14·7 „ |

This substance is to be regarded as the orthonitro-derivative of quinone-anilide—



Quinone-anilide.



Quinone-orthonitranilide.

### *Quinone-homofluorinidine.*

If the orthonitroquinoneanilide be heated under pressure with alcoholic ammonium sulphide to 100° C. in a close tube, colourless crystals are noticed, which are probably orthoamidoquinoneanilide. When these crystals are exposed to the air they become a bluish black colour.

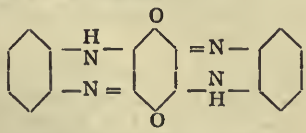
The mass is boiled with water and then re-crystallised from a mixture of methyl alcohol and benzene, from which mixture it separates in the form of dark green plates, which yield a violet-coloured powder having the same appearance as the homofluorindine of O. Fisher.

This blue colour and fluorescence with acetic acid, which is increased by adding a little alcohol, shows it to be a fluorindine. It is not, however, identical with homofluorinidine, as it containe oxygen.

On analysis it gave the following result:—

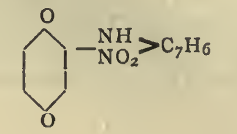
| | Found. | Theory, $C_{18}H_{10}N_4O_2$. |
|---|---|---|
| C .. .. | 68·5 p.c. | 68·7 p.c. |
| H .. .. | 3·9 „ | 2·3 „ |
| N .. .. | 17·7 „ | 17·8 „ |

Assuming it to be quinone-homofluorinidine it would have the following constitution:—

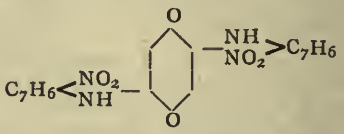


### *Orthonitrotoluidoquinone.*

When quinone and metanitroparatoluidine interact in a solution of glacial acetic acid the chief substance formed is a mononitrotoluidoquinone—



which yields a red crystalline mass when re-crystallised from absolute alcohol, while the dinitro-compound—



crystallises in bronze-coloured leaves and is harder to dissolve in absolute alcohol. The ortho-nitro compound decomposes at about 300° C.

| | Found. | Theory, $C_{13}H_{10}N_2O_4$. |
|---|---|---|
| N .. .. | 11·03 p.c. | 10·85 p.c, |

The dinitrotoluidoquinone decomposes at 140° C.

| | Found. | Theory, $C_{20}H_{16}N_4O_6$. |
|---|---|---|
| N .. .. | 13·6 p.c. | 13·7 p.c. |

(To be continued).

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

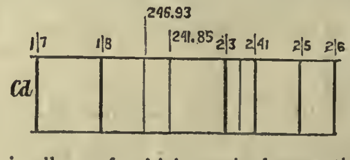
By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 252).

I obtained still stronger films in a similar manner, but with the difference that I removed them from the plate after drying; and as they were not quite uniform among themselves, I sought them out of a suitable thickness with the aid of the above-mentioned micrometer; cut them in slips of 0·5 m.m. in width, and fixed these slips in series, according to their thickness, across the slit—5 m.m. long and 1 m.m. wide—of a small opaque screen, and at a mutual distance of 1 m.m. In this manner there was formed a grating serving as a filter for the rays, the rods of which had the thickness of 0·13, 0·07, 0·058, 0·04, 0·03, 0·02, 0·01. When I covered the slit with this grating, each exposure gave seven different absorption spectra, separated from each other according to the distance of the neighbouring slips, by unenfeebled line-shaped spectra, which in reading off the data of absorption proved to be useful means of orientation. Three such proofs, each of a different time of exposure, were always produced on a plate of 20 m.m. in width. Such spectral series, on account of their compactness, afford an excellent general view. Even when magnified six times, all the forty-five spectra of such a plate can be brought simultaneously into the field of view.

Layer of gelatin, 0·13 m.m. in thickness. Cadmium sparks. Width of slit, 0·020 m.m. Length of exposure, 1, 4, 9 sparks, 1, 4, 9, 16 . . . 81.

The absorption extends to the entire ultra violet. It begins to a scarcely perceptible degree at the margin of the visible spectrum, increases gradually to the line 18, rises very rapidly from here, and reaches the maximum between the lines No. 18 and No. 23, close by the line 246·93 $\mu\mu$. This line appeared in all proofs which required more than nine seconds exposure, but invariably as a mere trace. Its intensity did not perceptibly increase even on an exposure of eighty-one seconds.



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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

Gelatin layer, 0·02 m.m. in thickness. Arrangement of the experiment exactly as in the 0·13 m.m. The absorption begins with the line No. 12, increases very gradually as far as the cadmium line 241·85 $\mu\mu$, and after a more rapid increase reaches its maximum near the wave-length 230·70 $\mu\mu$. The line No. 23 is of equal intensity in all exposures of longer than nine seconds, but it is everywhere very pale. The marginal line of these proofs, 230·70 $\mu\mu$, is rather more strongly deflected, but it can be recognised merely as a trace.

Gelatin layer, 0·01 m.m. in thickness. Arrangement of the experiment as in the foregoing. The transparence is here considerably greater than in the previous case. The absorption becomes perceptible only at the wave-length 288·01 $\mu\mu$. It increases at first slowly, but after 241·85 $\mu\mu$, rapidly. The most refrangible lines of these proofs merit especial attention. Up to No. 23 they are all very intense, but beyond No. 23, as also the line 230·70 $\mu\mu$, they again become strikingly pale and dim. The longest illumination, eighty-one seconds, led this time to a more intense and extensive proof. Hence it is prolonged rather further into the ultra-violet than all the rest. It ends with the line No. 24, wave-length 226·55 $\mu\mu$, which appears as a trace.

Layer of gelatin, 0·002 m.m. in thickness. Cadmium sparks. Width of slit, 0·010 and 0·020 m.m. Exposure, 1, 2, 3, 4, 5, 6 jar-sparks; 42, 4, 8, 16, 32, 96 seconds. The absorption begins with the line No. 17, scarcely increases perceptibly as far as No. 18, more strongly up to No. 23—on very short exposure No. 23 appears merely as a trace—and increases then so suddenly that all the lines only become efficient on prolonged exposure, but then powerfully. No. 24 concludes the spectrum, and—which is very uncommon—as a very intense line. There is not a trace of the refrangible lines Nos. 25 and 26.

Layer of gelatin of 0·001 m.m. in thickness. Cadmium and zinc sparks. Otherwise as for the thickness of 0·002 m.m. The transparence makes here notable advances. Up to No. 24 the spectrum appears almost in full force. Nos. 25 and 26, which were previously absent, now appear on short exposure, though feebly, and even the most refrangible lines of zinc can be traced to the last, which is a mere trace.

Layer of gelatin, 0·0004 m.m. in thickness. Zinc, aluminium, and tungsten sparks. Otherwise as at the thickness of 0·002. The absorption takes place quite uniformly, as is best shown with the tungsten spectrum. It begins with No. 23, is considerable at No. 27, increases from these progressively, and becomes complete near the aluminium line No. 30, traces of which may already be recognised.

Layer of gelatin, 0·00025 m.m. Zinc and aluminium sparks. Width of slit, 0·040 m.m. Exposure as for the thickness of 0·002 m.m.

The transparence extends strikingly further towards the more refrangible side. All the aluminium lines appear as traces, No. 32 stronger than the rest.

Layer of gelatin, 0·00008 in thickness. Aluminium, thallium, and tungsten sparks. Width of slit, 0·020 also 0·080 m.m. Exposure, 1, 2 jar-sparks; 1, 2, . . . 120 seconds. All the lines of aluminium appear paler than without the gelatin layer. The influence of absorption can be followed even in such thin films up to line No. 26.

(To be continued).

**The Nitrification of Meadow Soils.**—J. Dumont and J. Crochetelle.—The authors conclude from their researches that—(1) In soils rich in humus nitrification is intensified by the addition of small quantities of potassium carbonate (2 to 3 per 1000), but in larger doses the carbonate is injurious. (2) Potassium sulphate favours the production of nitrates in proportions of 7 to 8 parts per 1000. (3) Potassium chloride exerts only a moderate action. (4) Sodium carbonate does not appear to favour nitrification.—*Comptes Rendus*, cvii., No. 20.

# THE ACTION OF ZINC AND MAGNESIUM UPON METALLIC SOLUTIONS, AND THE DETERMINATION OF POTASSA.

By A. VILLIERS and F. BORG.

The electrolytic methods which enable us to determine, and often, indeed, to separate, metals are becoming more and more utilised in analytical chemistry. It seems, however, at first sight that we might in a great number of cases substitute for them a more rapid method, which consists in displacing metals by another metal, such as zinc or magnesium.

In reality, this latter procedure is applicable only in a very limited number of cases (copper, gold, platinum). The metals are not, in general, precipitated in a state of purity, but as alloys containing larger or smaller quantities of magnesium or zinc.

The proportion of these latter varies with the acidity of the liquids and with the weight of the metal employed. Another cause has also a remarkable influence upon this proportion—the degree of purity of the metal. It is thus that the weights of platinum displaced by equal weights of different specimens of zinc in equal volumes of one and the same solution of platinum chloride, have been 100·92, 100·39, 119·12 per cent; that is to say, the platinum has been precipitated with excesses of 0·92, 10·39, and 19·12 per cent. The first specimen of zinc had been obtained by the electrolysis of an ammoniacal solution of pure zinc sulphate; the second was a distilled zinc, containing no impurities except traces of sulphur not determinable by the balance; the third was commercial zinc, containing 1·1 per cent of impurities, of which 0·44 was fixed matter.

These results show that zinc cannot be used for the determination of platinum even after a correction for the impurities. When the zinc is impure, the presence of the impurities, even in an infinitely slight quantity, occasions the fixation of a very notable quantity of this metal upon the platinum. Electrolytic zinc gives results which are merely approximate.

Magnesium, as it is found in commerce in the form of ribbons, is, on the contrary, quite suitable for the determination of copper, gold, and platinum; and, consequently of potassium, after a precipitation as double platinum-potassium chloride.

*Determination of Copper.*—When copper is accompanied by no other metals except the alkaline and earthy metals, it may be determined very quickly and easily in the metallic state by treating its solutions with magnesium. The copper is thus liberated, in a slightly acid liquid, in the form of a granular precipitate very easy to wash. The washing is finished with alcohol; the metal is dried at 100° and weighed.

We may make use of a weighed filter, or more simply deposit the reduced copper in a small weighed capsule.

The process is not applicable in presence of metals like zinc easily acted on by hydrochloric acid; there are produced alloys even if the liquids are very acid.

*Determination of Potassium.*—If we determine potassium in the double platinum chloride, the precipitate is collected, after desiccation, on a weighed filter. Or we incinerate the filter, ignite the precipitate in hydrogen, and determine the platinum in the residue, after having removed the potassium chloride with water. The former method presents the causes of error inherent in the use of weighed filters. The latter method is tedious, and involves the successive incineration of two filters.

The following method is very rapid and very accurate. The double chloride, obtained in the ordinary manner, is washed with a mixture of equal volumes of alcohol and anhydrous ether, in the capsule in which it has been produced, until the filtrate runs through absolutely colourless—a result obtained with a small volume of the mixture. The residual salt is dissolved in boiling water, collecting the solution in a conical vessel. We add to it a little pure hydrochloric acid, and introduce gradually fragments of magnesium, until the liquor is completely decolourised and the magnesium dissolves without its surface becoming tarnished.

The platinum thus deposited is very easy to wash, and does not adhere to the sides of the capsule. It is brought upon a filter without folds; the filter, after desiccation, is incinerated, and the platinum is ignited. Its weight, multiplied by 0·3939 or by 0·4747, gives the corresponding weight of potassium or potassa.

This method is very advantageous in the determination of potassa in presence of soda and other substances, except ammoniacal salts. It is sufficient to substitute this method of liberating the platinum for that proposed by Corenwinder and Contamine in their method for the determination of potassa in mixtures such as salines or refined potash.

By the use of magnesium we have obtained exactly 100 per cent of the potassa contained in potassium sulphate mixed with large quantities of sodium phosphate and sulphate, calcium, magnesium, and iron chloride, and aluminium sulphate, if we employ for the precipitating and washing the chloroplatinate a mixture of equal volumes of anhydrous alcohol and ether.

In presence of bromides, the precipitate produced by platinum chloride may contain more or less bromine replacing an equivalent quantity of chlorine. Still, a determination of the weight of the platinum will give in this case an exact result.

We must not forget to transform the potassium salts into chloride if the acids are volatile, or, in the contrary case, to acidulate with hydrochloric acid.—*Bull. de la Soc. Chim. de Paris*, Series 3, ix. and x., p. 602.

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## THE INFLUENCE OF FREE NITRIC ACID AND AQUA REGIA ON THE PRECIPITATION OF BARIUM AS SULPHATE.*

By PHILIP E. BROWNING.

THE fact demonstrated by Dr. F. W. Mar (*Amer. Journ. Sci.*, xl., 283), in an interesting series of experiments, that free hydrochloric acid even in large quantities does not interfere with the complete precipitation of barium as sulphate when sulphuric acid is present in sufficient excess, but rather renders the precipitate more crystalline, and therefore more easily and quickly filtered, suggested a similar series of experiments having as their object an investigation of the influence of free nitric acid on the same precipitation. Certain qualitative preliminary experiments showed a similar effect to that brought about by hydrochloric acid as regards the crystalline form and rapid settling of the precipitate. It therefore remained to determine whether the nitric acid present had any solvent effect upon the precipitate. Accordingly a standard solution of barium nitrate was prepared, free from alkali, by precipitating a soluble barium salt with ammonium carbonate, washing thoroughly with hot water and dissolving in nitric acid, care being taken to avoid an excess of the acid, and making up to measure. Definite portions of this solution were drawn from a burette into counterpoised beakers, and weighed as a check on the burette reading. Several precipitations of the barium in the form of sulphate were made, both in the presence of free hydrochloric acid and in neutral solution, and the mean of closely agreeing determinations was taken as the value of the standard solution. The mode of procedure in the testing was simple and may be outlined as follows:—Into a counterpoised beaker a definite amount of the standardised solution of barium nitrate was drawn and the weight taken as before described; the amount of nitric acid to be used was then added, and the whole volume brought up to 90 c.m.$^3$ by the addition of water. This acid solution was then brought to the boiling point and 10 c.m.$^3$ of the dilute sulphuric acid added, and the whole was allowed to stand for the length of time shown by the Table before filtering on asbestos, igniting, and weighing. It will be seen that the total volume of liquid taken in each determination was uniformly 100 c.m.$^3$, the percentage of acid by volume being thus easily regulated. In no case did the amount of barium salt present exceed 0·4 grm. considered as the sulphate, and consequently the uniform amount of 10 c.m.$^3$ of dilute (1 : 4 by volume) sulphuric acid employed was always enough to assure the excess which Fresenius (*Zeitschr. f. Anal. Chem.*, xxx., 455) has shown to be necessary in the precipitation of barium as the sulphate in the presence of hydrochloric acid. By

SERIES I.

| | $BaSO_4$ equivalent to $Ba(NO_3)_2$ taken. | $BaSO_4$ found. | Error in terms of $BaSO_4$. | Averages. | Time between precipitation and filtration. | Per cent by volume of strong $HNO_3$. | Total volume. |
|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Hours. | | C.m.$^3$ |
| 1. | 0·2540 | 0·2336 | 0·0004 – | 0·0006 – | 12 | 5 | 100 |
| 2. | 0·2489 | 0·2483 | 6·0006 – | | ” | ” | ” |
| 3. | 0·2495 | 0·2489 | 0·0006 – | | ” | ” | ” |
| 4. | 0·2492 | 0·2482 | 0·0010 – | | ” | ” | ” |
| 5. | 0·2486 | 0·2483 | 0·0003 – | 0·0002 – | 6 | ” | ” |
| 6. | 0·2490 | 0·2490 | 0·0000 | | ” | ” | ” |
| 7. | 0·2555 | 0·2546 | 0·0009 – | 0·0006 – | 1 | ” | ” |
| 8. | 0·2538 | 0·2534 | 0·0004 – | | ” | ” | ” |
| 9. | 0·4067 | 0·4057 | 0·0010 – | 0·0006 – | 12 | 10 | ” |
| 10. | 0·2540 | 0·2533 | 0·0007 – | | ” | ” | ” |
| 11. | 0·2492 | 0·2489 | 0·0003 – | | ” | ” | ” |
| 12. | 0·2493 | 0·2488 | 0·0005 – | | ” | ” | ” |
| 13. | 0·2494 | 0·2488 | 0·0006 – | | ” | ” | ” |
| 14. | 0·2492 | 0·2492 | 0·0000 | 0·0002 – | 6 | ” | ” |
| 15. | 0·2490 | 0·2489 | 0·0001 – | | ” | ” | ” |
| 16. | 0·2489 | 0·2484 | 0·0005 – | | ” | ” | ” |
| 17. | 0·2540 | 0·2524 | 0·0016 – | 0·0016 – | 1 | ” | ” |
| 18. | 0·2529 | 0·2515 | 0·0014 – | 0·0007 – | 12 | 15 | 100 |
| 19. | 0·2534 | 0·2522 | 0·0012 – | | ” | ” | ” |
| 20. | 0·2533 | 0 2531 | 0·0002 – | | ” | ” | ” |
| 21. | 0·2538 | 0·2532 | 0·0006 – | | ” | ” | ” |
| 22. | 0·2497 | 0·2490 | 0·0007 – | | ” | ” | ” |
| 23. | 0·2489 | 0·2487 | 0·0002 – | | ” | ” | ” |
| 24. | 0·2542 | 0·2528 | 0·0014 – | 0·0006 – | 6 | ” | ” |
| 25. | 0·2486 | 0·2486 | 0·0000 | | ” | ” | ” |
| 26. | 0·2492 | 0·2487 | 0·0005 – | | ” | ” | ” |
| 27. | 0·2547 | 0·2532 | 0·0015 – | 0·0015 – | 1 | ” | ” |
| 28. | 0·2489 | 0·2478 | 0·0011 – | 0·0008 – | 12 | 20 | ” |
| 29. | 0·2486 | 0·2475 | 0·0011 – | | ” | ” | ” |
| 30. | 0·2548 | 0·2546 | 0·0002 – | | ” | ” | ” |
| 31. | 0·2548 | 0·2542 | 0·0006 – | | ” | ” | ” |
| 32. | 0·2496 | 0·2486 | 0·0010 – | | ” | ” | ” |
| 33. | 0·2539 | 0·2527 | 0·0012 – | 0·0008 – | 6 | ” | ” |
| 34. | 0·2488 | 0·2475 | 0·0013 – | | ” | ” | ” |
| 35. | 0·2497 | 0·2497 | 0·0000 | | ” | ” | ” |
| 36. | 0·2486 | 0·2477 | 0·0009 – | 0·0008 – | 12 | 25 | ” |
| 37. | 0·2491 | 0·2490 | 0·0001 – | | ” | ” | ” |
| 38. | 0·2494 | 0·2484 | 0·0010 – | | ” | ” | ” |
| 39. | 0·2538 | 0·2535 | 0·0003 – | | ” | ” | ” |
| 40. | 0·2492 | 0·2484 | 0·0008 – | | ” | ” | ” |
| 41. | 0·2487 | 0·2471 | 0·0016 – | | ” | ” | ” |
| 42. | 0·3414 | 0·3407 | 0·0007 – | | ” | ” | ” |
| 43. | 0·2489 | 0·2481 | 0·0008 – | 0·0007 – | 6 | ” | ” |
| 44. | 0·2485 | 0·2478 | 0·0007 – | | ” | ” | ” |

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* *American Journal of Science*, xlv., 1893.—Contributions from the Kent Chemical Laboratory of Yale College.

reference to Series I. it is evident that in the presence of 5 per cent of nitric acid very little solvent action is shown, and it appears also that the sulphate may be safely filtered after an hour's time. In the presence of 10 to 15 per cent of the acid the solvent effect is very small when the solution is allowed to stand six hours or more. With 20 to 25 per cent of acid present we find the solubility to be slightly increased, but even then the average loss is less than 0·001 grm.

### Series II.

| | BaSO$_4$ equivalent to Ba(NO$_3$)$_2$ taken. | BaSo$_4$ found. | Error in terms of BaSO$_4$. | Averages. | Time between precipitation and filtration. | Per cent by vol. of strong aqua regia. (3HCl : 1HNO$_3$. | Total volume. |
|---|---|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | Hours. | | C.m.$^3$ |
| 1. | 0·2539 | 0·2534 | 0·0005 − | 0·0002 − | 12 | 5 | 100 |
| 2. | 0·2540 | 0·2538 | 0·0002 − | | ,, | ,, | ,, |
| 3. | 0·2490 | 0·2490 | 0·0000 | | ,, | ,, | ,, |
| 4. | 0·2491 | 0·2492 | 0·0001 + | 0·0001 − | ,, | ,, | ,, |
| 5. | 0·2488 | 0·2484 | 0·0004 − | | 6 | ,, | ,, |
| 6. | 0·3419 | 0·3421 | 0·0002 + | | ,, | ,, | ,, |
| 7. | 0·2491 | 0·2487 | 0·0004 − | 0·0006 − | 12 | 10 | ,, |
| 8. | 0·2486 | 0·2482 | 0·0004 − | | ,, | ,, | ,, |
| 9. | 0·2549 | 0·2539 | 0·0010 − | | ,, | ,, | ,, |
| 10. | 0·2543 | 0·2538 | 0·0005 − | | ,, | ,, | ,, |
| 11. | 0·2487 | 0·2485 | 0·0002 − | 0·0002 − | 6 | ,, | ,, |
| 12. | 0·3416 | 0·3415 | 0·0001 − | | ,, | ,, | ,, |
| 13. | 0·3417 | 0·3420 | 0·0003 + | 0·0003 + | 1 | ,, | ,, |
| 14. | 0·2547 | 0·2544 | 0·0003 − | 0·0003 − | 12 | 15 | ,, |
| 15. | 0·2492 | 0·2492 | 0·9000 | | ,, | ,, | ,, |
| 16. | 0·2489 | 0·2479 | 0·0010 − | | ,, | ,, | ,, |
| 17. | 0·3412 | 0·3412 | 0·0000 | | ,, | ,, | ,, |
| 18. | 0·3418 | 0·3417 | 0·0001 − | 0·0001 − | 6 | ,, | ,, |
| 19. | 0·3413 | 0·3412 | 0·0001 − | | ,, | ,, | ,, |
| 20. | 0·3411 | 0·3402 | 0·0009 − | 0·0009 − | 1 | ,, | ,, |
| 21. | 0·2492 | 0·2484 | 0·0008 − | 0·0005 − | 12 | 20 | ,, |
| 22. | 0·2486 | 0·2480 | 0·0006 − | | ,, | ,, | ,, |
| 23. | 0·2491 | 0·2485 | 0·0006 − | | ,, | ,, | ,, |
| 24. | 0·3412 | 0·3411 | 0·0001 − | | ,, | ,, | ,, |
| 25. | 0·3417 | 0·3418 | 0·0001 + | 0·0000 − | 6 | ,, | ,, |
| 26. | 0·3417 | 0·3417 | 0·0000 | | ,, | ,, | ,, |
| 27. | 0·3414 | 0·3404 | 0·0010 − | 0·0010 − | 1 | ,, | ,, |
| 28. | 0·2491 | 0·2485 | 0·0006 − | 0·0003 − | 12 | 25 | ,, |
| 29. | 0·1701 | 0·1697 | 0·0004 − | | ,, | ,, | ,, |
| 30. | 0·1708 | 0·1705 | 0·0003 − | | ,, | ,, | ,, |
| 31. | 0·1710 | 0·1710 | 0·0000 | | ,, | ,, | ,, |
| 32. | 0·3415 | 0·3410 | 0·0005 − | 0·0003 − | 6 | ,, | ,, |
| 33. | 0·3418 | 0·3418 | 0·0000 | | ,, | ,, | ,, |
| 34. | 0·3412 | 0·3405 | 0·0007 − | 0·0007 − | 1 | ,, | ,, |

### Series III.

| Impurity present to the amount of 5 grms. | BaSO$_4$ equivalent to Ba(NO$_3$)$_2$ taken. | Apparent amount of BaSO$_4$ found. | BaSO$_4$ after purification. | Error after purification. | Percentage of strong HNO$_3$ by volume. |
|---|---|---|---|---|---|
| | Grm. | Grm. | Grm. | Grm. | |
| 1. Ammonium nitrate | 0·1710 | 0·1800 | 0·1702 | 0·0008 − | 10 |
| 2. ,, ,, | 0·3415 | 0·3440 | 0·3410 | 0·0005 − | ,, |
| 3. ,, citrate | 0·3412 | 0·3442 | 0·3407 | 0·0005 − | ,, |
| 4. Sodium ,, | 0·1360 | 0·1730 | 0·1366 | 0·0006 + | ,, |
| 5. Metaphosph. acid .. | 0·3461 | 0·3511 | 0·3470 | 0·0009 + | ,, |

Having shown that free nitric acid, even though present in considerable amount, has only a slight solvent influence upon barium sulphate, it seemed interesting to try the effect of the combination of nitric and hydrochloric acids mixed in the proportion to form aqua regia ($3HCl:1HNO_3$). The experiments recorded in Series II. show that aqua regia has even less effect as a solvent than nitric acid alone. In fact it seems to act like hydrochloric acid alone, which practically has no solvent effect, as shown by Dr. Mar's work previously cited.

In this connection I append the results of a few experiments made to determine the effect of the presence of a considerable amount of free nitric acid, on the precipitations of barium as sulphate in cases where certain substances are present which under ordinary conditions tend to hold up the precipitate. Fresenius (*Zeitschr. f. Anal. Chem.* ix., 62) has demonstrated this property in the case of ammonium nitrate, Scheerer and Rube (*Journ. Prakt. Chem.* lxxv, 113—116) have shown that metaphosphoric acid acts similarly, and Spiller (Chem. News. viii., 280—281) notes the same general effect where alkaline citrates are present. Series III. shows the results obtained by precipitating definite portions of the standard solution of barium nitrate in the presence of stated amounts of the substances just mentioned. The total volume in every case was 100 c.m.$^3$, the amount of dilute sulphuric acid used 10 c.m.$^3$, and the time between precipitation and filtration twelve hours. Upon filtering, igniting, and weighing the barium sulphate, an excess of weight, due undoubtedly to contamination of the precipitate, was found. It became necessary, therefore, to purify the precipitate as first weighed in order to determine whether all the barium was actually precipitated or whether a partial loss was covered by the amount of included impurity. The method of purification employed was that successfully applied by Dr. Mar in the work previously mentioned. The contaminated sulphate, collected on paper and treated according to the familiar method (on account of the difficulty attending the complete removal of the precipitate from asbestos for purposes of purification), was dissolved in warm concentrated sulphuric acid, and evaporated quickly and without spattering by means of the Hempel burner, the barium sulphate being left after this treatment in coarse granular crystals. The crystallised sulphate was warmed with a little water containing a drop of sulphuric acid, filtered upon an asbestos felt contained in a perforated platinum crucible, the crucible and felt having been previously ignited and weighed.

The results show that in the presence of nitric acid amounting to one-tenth by volume of the entire liquid these salts exert no apparent interference with the precipitation of the barium.

The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to 10 per cent by volume of the liquid treated is not only not to be avoided in estimating barium as the sulphate, but is actually beneficial. Ordinarily the advantage is found in the tendency of the precipitate to fall coarsely crystalline under the conditions. In certain special cases in which certain substances mentioned, which would otherwise exert solvent action, are present, the precipitation is made complete. The contaminating effect of such substances when complete precipitation is induced may be corrected by dissolving the precipitate in sulphuric acid and recrystallising by evaporation.

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**Royal Institution.**—The annual Christmas Course of Lectures for Children will this year be delivered by Prof. James Dewar, F.R.S. The subject will be "Air, Gaseous and Liquid," and the first lecture will be delivered in the theatre of the Royal Institution, Albemarle Street, on Thursday, December 28. The next General Monthly Meeting of the Members will take place on Monday next at 5 o'clock.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, November 2nd*, 1893.

Dr. Armstrong, President, in the Chair.

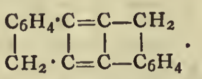
(Concluded from p. 255).

*67. "*The Formation of the Hydrocarbon 'Truxene' from Phenylpropionic Acid and from Hydrindone.*" By F. Stanley Kipping, Ph.D., D.Sc.

The further study of the hydrocarbon obtained from phenylpropionic acid (*Proc. Chem. Soc.*, cxii., 107; cxvii., 216) has led to the following results:—

The hydrocarbon is formed when hydrindone is heated either with phosphoric anhydride or with moderately concentrated sulphuric acid; it is also produced when a condensation product of hydrindone of the composition $C_{18}H_{14}O$ is heated with either of these dehydrating agents.

This condensation product will be described in a future paper; the fact that it is readily converted into the hydrocarbon proves that the latter has the formula $C_{18}H_{12}$, and not $C_{27}H_{18}$, and is also evidence in favour of the view that the constitution of the hydrocarbon is expressed by the formula—



$$\begin{array}{l} C_6H_4\cdot C{=}C{-}CH_2 \\ \;|\qquad\;\; |\quad\; |\quad\;\; | \\ CH_2\cdot C{=}C{-}C_6H_4 \end{array} .$$

This view affords a simple explanation of the formation of the hydrocarbon from phenylpropionic acid and of its relation to other compounds.

The hydrocarbon in question is evidently identical with a compound obtained by Hausmann (*Ber.*, xxii., 2019) by heating hydrindone with concentrated chlorhydric acid, the study of which he did not continue. It is also identical with "truxene," a hydrocarbon prepared by Liebermann and Bergami (*Ber.*, xxii., 782) by reducing "truxone" with iodhydric acid; this is proved by the fact that both compounds are converted into Gabriel and Michael's "tribenzoylenebenzene" (*Ber.*, x., 1557) on oxidation with chromic acid.

The author discusses the constitution of "truxene" and of "truxone," and points out that the formulæ assigned to them by Liebermann and Bergami (*Ber.*, xxiii., 317) do not accord with the facts of the case, and are not to be reconciled with the formation of truxone from α-truxillic acid, $C_{18}H_{16}O_4$. It is also shown that the only evidence which led Liebermann and Bergami to assume that "truxene" is a "tribenzylenebenzene," namely, its conversion into "tribenzoylenebenzene," is of little, if of any, value.

The constitution of "tribenzoylenebenzene," being based on its conversion into triphenylbenzene, cannot be regarded as established, as it is first fused with potash at a high temperature and the product of this treatment is distilled over lime in order to bring about the change. It follows, therefore, that the conversion of the hydrocarbon from phenylpropionic acid into "tribenzoylenebenzene" does not show that the former (truxene) has the molecular formula $C_{27}H_{18}$, but that "tribenzoylenebenzene," which was hitherto supposed to have the molecular formula $C_{27}H_{12}O_3$, is, in reality, $C_{18}H_8O_2$; this view is not refuted, but is rather corroborated by a study of the methods of forming "tribenzoylenebenzene."

The behaviour of truxene with nitric acid and with bromine and its oxidation to nitrophthalic acid—

$$[2COOH : NO_2 = 1 : 2 : 4]$$

are described; attention is also drawn to a characteristic colouration which the hydrocarbon gives with ordinary concentrated sulphuric acid, and to its very peculiar decomposition by boiling nitrobenzene.

68. "*The Action of Aluminium Chloride on Heptylic Chloride.*" By F. Stanley Kipping, Ph.D., D.Sc.

The fact that hydrindone is formed in large quantities on treating phenylpropionic chloride with aluminium chloride (*Proc. Chem. Soc.*, cxvii., 216) led the author to investigate the action of the latter on heptylic chloride, as it appeared possible that methylketohexamethylene, ethylketopentamethylene, or some other closed-chain compound might be formed.

After many unsuccessful experiments, in which almost the whole of the heptylic chloride was recovered as heptylic acid, it was found that under suitable conditions a large proportion of the acid chloride was converted into a neutral oil which was isolated by distillation in steam, but which proved to be a mixture; on cooling the fractions of highest boiling-point collected between 290° and 310°, a considerable quantity of colourless crystals was deposited which, when freed from oil, melted at about 41°. Analyses of this crystalline product gave results (I., C = 82·2, H = 10·2; II., C = 82·0, H = 10·0 per cent) corresponding to the formula—

$$C_{14}H_{20}O = 2C_6H_{13}\cdot COCl - 2HCl - H_2O - H_2.$$

It yields an oily hydroxime. On analysing this (found C = 75·4, H = 10·0, N = 6·7; required C = 76·7, H = 9·6, N = 6·4), the percentage of carbon found was somewhat lower than corresponds to the formula $C_{14}H_{20}NOH$, doubtless owing to the fact that the oil could not be purified.

It would seem, therefore, that the crystalline substance is a *ketone*, as was, in fact, to be expected.

The experiments which have been carried out up to the present with the object of determining its constitution, although few in number, have already afforded results of considerable interest. Fractions of the crude oil collected between 280° and 310°, when oxidised with nitric acid, gave a mixture of several acids, one of which was characterised by sparing solubility, and was, therefore, easily isolated; analyses of this *acid* gave results pointing to the formula $C_{13}H_{10}O_6$ (found C = 59·4, H = 3·9; required C = 59·5, H = 3·8), and an analysis of its *silver salt*, $C_{13}H_7O_6Ag_3$ (found Ag = 55·1; required 55·5 per cent) confirmed this view. Whether this acid is an oxidation product of the ketone $C_{14}H_{20}O$, or whether it is produced from some other constituent of the oil, has not yet been determined, but in any case its indirect formation from heptylic acid is cetainly rather extraordinary, as, to judge from its composition, it is a closed-chain compound.

The investigation of the behaviour of acid chlorides with aluminium chloride is being extended, and some progress has already been made with experiments with the chlorides of butyric, benzoylpropionic, and hippuric acids.

*69. "*The Inertness of Quicklime. II. The Interaction of Chlorine and Lime.*" By V. H. Veley.

The author has ascertained by synthetical and analytical methods that no appreciable action takes place between dry chlorine and quicklime below 300°; above this temperature a partial displacement of oxygen is effected by the chlorine: the interaction is thus analogous to that of baryta and chlorine not specially dried and at ordinary temperatures.

*70. "*Note on Hyponitrites.*" By D. H. Jackson, M.A., B.Sc.

The author has conducted experiments for the purpose of obtaining alkali hyponitrites, hitherto known only in solution, in a solid state. He confirms the experience of previous observers that, contrary to the statement of Menke, hyponitrite is not formed when sodium nitrate is heated with metallic iron. Reduction of a solution of sodium nitrate with aluminium or with barium amalgam does not furnish hyponitrite. For the production of hyponitrites, the author employs Divers' method of reducing a solution of sodium nitrate with sodium amalgam. He finds that the best yield of hyponitrite results from the use of an amalgam weak in sodium acting at a low temperature; owing to the violence of the action, no hyponitrite is obtained when sodium alone is used as the reducing agent. The origin of the metallic silver which generally contaminates silver hyponitrite produced by the usual process is traced to the reduction of silver hyponitrite by the hydroxylamine acetate contained in the solution in which precipitation is effected. In order to avoid loss of hyponitrite from this cause, it is recommended to add mercuric oxide to the alkaline solution resulting from the reduction. This destroys the hydroxylamine, and therefore the silver hyponitrite subsequently produced does not darken in the liquid. Although an aqueous solution of sodium hyponitrite quickly decomposes into sodium hydroxide and nitrous oxide, it was found that in the presence of much sodium hydroxide considerably less decomposition takes place. A strongly alkaline solution of sodium hyponitrite, prepared by reducing a strong solution of sodium nitrate, when spontaneously evaporated over sulphuric acid in a vacuum during several weeks, deposited crystals of sodium hyponitrite, which could be freed from hydroxide by washing with alcohol, in which the hyponitrite is very sparingly soluble. The crystals may also be obtained by precipitating a strong aqueous solution of the salt prepared by the interaction of silver hyponitrite and sodium chloride with alcohol. A determination of the sodium in these crystals showed that they possessed the composition of sodium hyponitrite.

Ammonium hyponitrite was obtained in groups of long needles by decomposing silver hyponitrite with an alcoholic solution of ammonium sulphide, and evaporating the filtered liquid over sulphuric acid in a vacuum. Like the sodium salt, this compound is difficult to obtain in any quantity, and this circumstance prevented the author from further investigating the properties of these hyponitrites.

71. "*The Interaction of Hydrogen Chloride and Potassium Chlorate.*" By W. H. Pendlebury, M.A., and Mrs. McKillop.

The authors have determined the amount of oxidising gases (whether chlorine or its oxides) removed on passing a given volume of air at a given rate through an aqueous solution of potassium chlorate and hydrogen chloride kept at a constant temperature, and have compared the amount removed with that present in the liquid. The evolved gases were received in a solution of potassium iodide, and at the end of each half hour the amount of iodine liberated was determined.

The following results were obtained at 30° with a mixture containing 30 grms. of potassium chlorate and 18·823 grms. of hydrogen chloride in 800 c.c.; the half-hourly determination of iodine was not performed during 41⅛ hours, 5·5 hours after mixing.

| Hours after mixing. | Mass of iodine liberated. | Hours after mixing. | Mass of iodine liberated. |
|---|---|---|---|
| 2·0 | 0·0021 | 47·5 | 0·0028 |
| 2·5 | 0·0032 | 48·0 | 0·0025 |
| 3·0 | 0·0038 | 48·5 | 0·0022 |
| 3·5 | 0·0035 | 68·0 | 0·0012 |
| 4·0 | 0·0034 | 69·0 | 0·0015 |
| 4·5 | 0·0028 | 69·5 | 0·0016 |
| 5·0 | 0·0025 | 70·0 | 0·0015 |
| 5·5 | 0·0022 | 71·5 | 0·0016 |
| 47·0 | 0·0023 | 72·0 | 0·0015 |

In a second set of observations twice the amount of hydrogen chloride was used ($KClO_3 : 4HCl$) (see first Table, next column).

100 c.c. portions were withdrawn at regular intervals from a solution of the same strength as that used in the second set of experiments kept at 30°, and the amount of iodine liberated thereby was ascertained.

A comparison of the two sets of observations shows that only a portion of the oxidising gases is removed by the passage of the air.

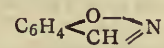
| Hours after mixing. | Mass of iodine liberated. | | Hours after mixing. | Mass of iodine liberated. | |
|---|---|---|---|---|---|
| 0·5 | 0·012 | | 35·0 | 0·042 | |
| 1·0 | 0·017 | | 40·0 | 0·048 | |
| 1·5 | 0·018 | | 44·5 | 0·045 | |
| 2·0 | 0·022 | 0·026 | 45·0 | 0·040 | |
| 2·5 | 0·026 | | 45·5 | 0·040 | |
| 3·0 | 0·022 | | 50·0 | 0·039 | |
| 3·5 | 0·024 | | 53·5 | 0·030 | 0·31 |
| 4·0 | 0·028 | | 54·0 | 0·033 | |
| 4·5 | 0·026 | | 65·0 | 0·030 | |
| 5·0 | 0·029 | | 65·5 | 0·032 | |
| 5·5 | 0·024 | | 66·0 | 0·030 | |
| 6·0 | 0·029 | | 66·5 | 0·031 | |
| 6·5 | 0·028 | | 70·0 | 0·032 | |
| 24 | 0·042 | | 90·0 | 0·033 | |

| Hours after mixing. | Iodine liberated. | Hours after mixing. | Iodine liberated. |
|---|---|---|---|
| 1 | 0·0021 | 24 | 0·0031 |
| 2 | 0·0022 | 28 | 0·0036 |
| 3 | 0·0024 | 29 | 0·0036 |
| 4 | 0·0022 | 31 | 0·0041 |
| 5 | 0·0023 | 32 | 0·0041 |
| 6 | 0·0024 | 46 | 0·0055 |
| 7 | 0·0029 | 47 | 0·0054 |
| 8 | 0·0033 | 76 | 0·0045 |
| 22 | 0·0032 | 77 | 0·0045 |
| 23 | 0·0031 | 94 | 0·0047 |

Observations are referred to showing that a solution —such as was used in these experiments—which, after exposure during forty-six hours in subdued light, liberated iodine to the extent of 0·0055 grm. per 10 c.c., after exposure at a window to bright sunlight during thirty minutes, liberated only 0·0038 grm. per 10 c.c.; after one hour's exposure the amount liberated had fallen to 0·0023, but no further reduction took place after three hours and a half's exposure. On removal into subdued light, the iodine-liberating power increased, being 0·0035 after four hours, and rising to 0·0048 after twenty hours in the dark. As solutions of the oxides of chlorine lose in oxidising power on exposure to light, the change observed in the chlorate solution is probably due to their destruction.

72. "*The Formation of Indoxazen Derivatives.*" By Wm. A. Bone, Ph.D.

The author has investigated the behaviour of orthochloronitrobenzaldoxime towards alkalis with a view to isolating nitrindoxazen,—



$$C_6H_4<\begin{matrix} O\text{—} \\ CH \end{matrix}\gg N.$$

Orthochlorobenzal chloride was converted by the action of fuming sulphuric acid into the corresponding aldehyd, which was then nitrated, and the nitrated aldehyd was converted into the hydroxime; on subjecting this to the action of caustic potash at 130°, ammonia was evolved, and hydrogen chloride was split off. On acidifying the solution, a white precipitate was thrown down, which, after re-crystallisation, melted at 222°; it possessed acid properties, and gave a red colour with ferric chloride solution. Analysis of the silver salt showed it to be 1 : 2 : 5-nitro salicylic acid.

The hydroxime was then heated at 120° with a solution of sodium carbonate; hydrogen chloride was split off, but no ammonia was evolved. On acidifying the liquid, beautiful yellow needles appeared, melting at 189°.

The properties of the product (especially the facts that it gave a red colour with ferric chloride, and on heating with caustic potash yielded 1 : 2 : 5-nitrosalicylic) pointed to the conclusion that it was 1 : 2 : 5-nitrosalicylonitril, isomeric with nitrindoxazen, a molecular change having occurred during the interaction. In order to decide the question, the hitherto unknown nitriles of 1 : 2 : 5-nitrosalicylic acid were investigated. Several attempts were unsuccessfully made to prepare these by well-known interactions; at last, by heating salicylaldoxime with acetic anhydride, and subsequently hydrolysing with dilute caustic potash, an almost quantitative yield of salicylonitril was obtained.

On nitrating salicyonitrile with fuming nitric acid, the 1 : 2 : 3 : 5-dinitronitril was obtained crystallised in yellow plates, melting at 175°; unlike other members of the salicylic series, it gave no colouration with ferric chloride.

On using ordinary nitric acid, and conducting the nitration below 0°, the 1 : 2 : 5-mononitronitril was obtained. This crystallises in long pale yellow needles melting at 190°; it gave a red colouration with ferric chloride, and was found to be identical with the product obtained from orthochloronitrobenzaldoxime and sodium carbonate.

Derivatives of these nitriles were prepared and studied, notably their amidoximes. That of the mononitronitril is a weak base; its hydrochloride crystallises in yellow tablets melting at 215°. That of the dinitronitril is a neutral substance, crystallising in orange tablets melting at 204°.

The author, finally, attempted to prepare nitromethylindoxazen. Indoxazen itself is evidently exceedingly unstable, but it was thought that a methyl derivative would be more stable, and it seemed likely that orthochloronitracetophenoxime would yield nitromethylindoxazen.

The hitherto unknown orthochloracetophenone was prepared by the action of orthochlorobenzoyl chloride on ethylic acetosodacetate, and subsequently hydrolysing the product. All attempts to prepare orthochloronitracetophenone from this failed, however, owing to the fact that nitration was accompanied by simultaneous oxidation.

Orthochloracetophenone is a colourless oil which boils at 235—240°.

Orthochloronitracetophenone was prepared by the action of orthochloronitrobenzoyl chloride on ethylic acetosodacetate, and subsequently hydrolysing the product. It is a very thick syrup, becoming crystalline on standing. The author was unsuccessful in preparing the hydroxime from this, although experiments were made under various conditions (at ordinary temperatures, at 100°, and under pressure at 130°); in all cases the ketone was unaltered, owing, probably, to the very negative character of the $C_6H_3(NO_2)Cl$ group.

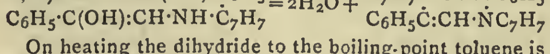
73. "*The Interaction of Benzylamine and Phenacyl Bromide. Synthesis of Piazine Derivatives.*" By Arthur T. Mason, Ph D., and Goodlatte Winder, Ph.D.

Phenacyl bromide and benzylamine easily interact, forming monophenacylbenzylamine,—

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}Ph,$$

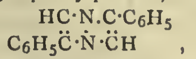
and diphenacylbenzylamine, $(Ph{\cdot}CO{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}Ph$.

These compounds were isolated in the form of hydrobromides, as on setting the bases free molecular changes take place; in the case of monophenacylbenzoylamine, 2 molecules combine to form 1 : 4-dibenzyl-2 : 5-diphenylpiazine dihydride, the condensation being analogous to that which takes place in the case of isoamidoacetophenone :—



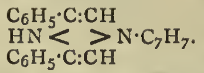
$$\begin{array}{l} C_7H_7{\cdot}NH{\cdot}CH{:}C(OH){\cdot}C_6H_5 \\ C_6H_5{\cdot}C(OH){:}CH{\cdot}NH{\cdot}\dot{C}_7H_7 \end{array} = 2H_2O + \begin{array}{l} C_7H_7N{\cdot}CH{:}CC_6H_5 \\ C_6H_5\dot{C}{:}CH{\cdot}\dot{N}C_7H_7 \end{array}$$

On heating the dihydride to the boiling-point toluene is eliminated and 2 : 5-diphenylpiazine,—



$$\begin{array}{r} HC{\cdot}N.C{\cdot}C_6H_5 \\ C_6H_5\ddot{C}{\cdot}\dot{N}{\cdot}\ddot{C}H \end{array},$$

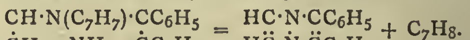
is formed, the product being identical with that from isoamidoacetophenone (*Ber.*, xxi., 1269). When diphenacylbenzylamine is set free it is probably converted into an oxazine derivative. Cold alcoholic ammonia converts the hydrobromide of diphenacylbenzylamine quantitatively into an amide, $(C_6H_5{\cdot}C(OH){:}CH)_2N{\cdot}C_7H_7$, which, at 100°, loses one molecule of water, 2 : 6-diphenyl-4-benzylpiazine dihydride being formed,—



$$HN \begin{array}{l} C_6H_5{\cdot}C{:}CH \\ < \quad > \\ C_6H_5{\cdot}C{:}CH \end{array} N{\cdot}C_7H_7.$$

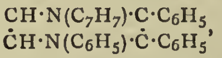
The same condensation occurs on warming the amide with dilute chlorhydric acid, the hydrochloride of the dihydride being formed.

When further heated, the hydride, as well as its hydrochloride, yields 2 : 6-diphenylpiazine, toluene, or benzyl chloride, as the case may be, being eliminated.



$$\begin{array}{l} CH{\cdot}N(C_7H_7){\cdot}CC_6H_5 \\ \dot{C}H - NH - \dot{C}C_6H_5 \end{array} = \begin{array}{l} HC{\cdot}N{\cdot}CC_6H_5 \\ H\ddot{C}{\cdot}\dot{N}{\cdot}\ddot{C}C_6H_5 \end{array} + C_7H_8.$$

Aniline and benzylamine act on diphenacylbenzylamine hydrobromide, forming the dihydride,—



$$\begin{array}{l} CH{\cdot}N(C_7H_7){\cdot}C{\cdot}C_6H_5 \\ \dot{C}H{\cdot}N(C_6H_5){\cdot}\dot{C}{\cdot}C_6H_5 \end{array},$$

and 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride.

On heating the latter compound with concentrated chlorhydric acid at 170°, two atoms of hydrogen are eliminated; the product is devoid of basic properties and unaltered by benzoyl chloride and acetic anhydride, and is probably 2 : 6-diphenyl-3 : 5-dibenzylpiazine. If, however, 1 : 4-dibenzyl-2 : 6-diphenylpiazine dihydride be heated alone at 260—270°, toluene is eliminated, and the remaining benzyl radicle probably "wanders" from nitrogen to carbon, 2 : 6-diphenyl-3-benzylpiazine being found.

These transformations are comparable with those occurring when toluidine and xylidine are formed by heating the hydrochlorides of monomethyl- and dimethylaniline.

On treating the dihydride with an alcoholic solution of ferric chloride and chlorhydric acid, it yields 2 : 6-diphenyl-4-benzylpiazine dihydride.

74. "*The Interaction of Quinones and Metanitraniline and Nitroparatoluidine.*" A Preliminary Note. By James Leicester, Ph.D.

The relationship between quinonedianilide and azophenine has been pointed out by O. Fischer and E. Hepp (*Ber.*, 1888, 683), who also prepared fluorindine from the latter compound (*Ber.*, 1890, 2789).

In a previous paper (*Ber.*, 1890, 2793); *Proc. Chem. Soc.*, Abstracts, 1890, 1445) I gave the results of an investigation of the action of orthonitraniline and metanitroparatoluidine on quinone, toluquinone, and naphthaquinone, and showed that in principle the interaction was the same as in the case of aniline and quinone; for example, orthonitraniline and quinone combine to form quinonediorthonitranilide,—

$$C_6H_2O_2(NHC_6H_4NO_2)_2\ [CO : NH = 1 : 2 : 4 : 5],$$

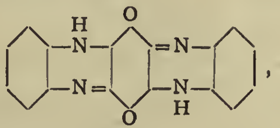
which on reduction with ammonium sulphide yields quinonehomofluorindine.

In addition to the quinonefluorindines, certain quinonephenazine derivatives were obtained; these are formed from the nitro-compounds corresponding to quinoneanilide, quinoneorthonitrotoluide - yielding quinoneorthomethylphenazine. I have now prepared a number of other quinonephenazines and quinonefluorindines; in fact, the interaction appears to be a general one in the case of paraquinones. The constitution of these compounds may be inferred partly from the manner in which they are formed and partly from their similarity in properties to the corresponding fluorindines. A number of crystalline compounds have also been obtained by the reduction of the anilides and toluides with magnesium; the products are, however, of a somewhat complex nature and their further investigation is proceeding.

Quinonedimetanitranilide is prepared by heating a solution of quinone and metanitraniline in glacial acetic acid; it crystallises from a mixture of methyl alcohol and benzene, and melts at 295°.

Quinonemetanitranilide is obtained together with the dianilide as a bronze-coloured powder melting at 135°.

Quinonemetahomofluorindine,—

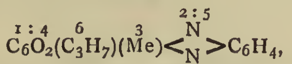


is formed by the reduction of the dianilide with ammonium sulphide; it is a brownish black powder melting above 360°. It affords a brown colour with acetic acid, changes to slaty green, and finally to mauve, on the gradual addition of sulphuric acid.

Quinoneparanitrotoluide is obtained in a similar manner as a bluish black crystalline powder; on reduction with ammonium sulphide it yields a slate-coloured compound which decomposes at about 300°.

Quinonediparanitrotoluide is a bronze-coloured substance; on reduction it yields a substance which melts at 320°, and dissolves in alcohol, benzene, or acetic acid, forming a dark greenish yellow coloured liquid, exhibiting a green fluorescence.

Thymoquindiorthonitranilide, from thymoquinone and orthonitraniline, crystallises from alcohol and ether in straw-coloured needles melting at 125°. The phenazine,—

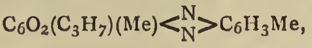


$$\overset{1:4}{C_6O_2}(\overset{6}{C_3H_7})(\overset{3}{Me}){<}\overset{\overset{2:5}{N}}{\underset{N}{}}{>}C_6H_4,$$

derived from it, forms grey needles melting at about 320°.

Thimoquindiparanitrotoluide is deposited from absolute alcohol in yellowish red plates melting at 112°; it also crystallises in needles.

Thymoquinorthomethylphenazine,

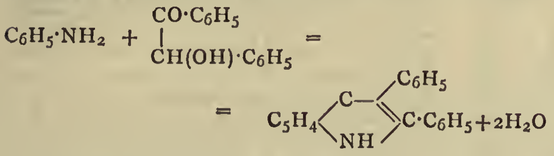


$$C_6O_2(C_3H_7)(Me){<}^{N}_{N}{>}C_6H_3Me,$$

is a greyish white crystalline powder which sublimes at 325°, and dissolves in acetic acid and ether, forming a yellow coloured liquid.

75. "*Preparation of α-β-Diphenylindoles from Benzoïn and Primary Benzenoid Amines.*" By R. Japp, F.R.S., and T. S. Murray, D.Sc.

The authors have found that a mixture of benzoïn, aniline, and zinc chloride yields E. Fischer's α-β-diphenylindole according to the equation—



By employing in place of aniline, orthotoluidine, paratoluidine, α-naphthylamine, and β-naphthylamine, they obtained respectively α-β-diphenylorthotoluindole (m. p. 136°), α β-diphenylparatoluindole (m. p. 153°), α-β-diphenyl-α-naphthindole (m. p. 141°), and α-β-diphenyl-β-naphthindole (m. p. 166°).

Their work had proceeded thus far when a paper appeared by Bischler and Fireman (*Ber.*, xxvi., 1336), in which the preparation of these indoles (with the exception of α-β-diphenyl-α-naphthindole) by a different method was described. This method consists in first acting on cold desyl bromide with a primary benzenoid amine so as to obtain a desylanilide, thus,—

$$C_6H_5{\cdot}CO{\cdot}CH(NHC_6H_5){\cdot}C_6H_5,$$

and then boiling this compound with an excess of amine, when, according to Bischler and Fireman, it is converted into an indole.

The authors now show :—

1. That the desylanilides described as new by Bischler and Fireman are, in reality, identical with the anilbenzoin series obtained by Voigt (*J. Pr. Chem.*, [2], xxxiv., 2) by heating benzoin with aniline, paratoluidine, and β-naphthylamine respectively. The constitution assigned to the compounds by Bischler and Fireman, which differs from that given by Voigt, is, however, correct.

2. That these desylanilides, contrary to the statement of Bischler and Fireman, are not converted into indoles by boiling them with amines. In order that this transformation may occur, it is necessary that the hydrochloride or hydrobromide of the amine should also be present. The desylanilides used by these authors were, from the mode of preparation, doubtless contaminated with aniline hydrobromide.

3. That the foregoing indoles, with the exception of α-β-diphenyl-β-naphthindole can be most readily obtained by boiling benzoin with a mixture of primary benzenoid amine and its hydrochloride. α-β-Diphenyl-β naphthindole is best prepared by the zinc chloride method.

The authors also find that all these indoles when crystallised from acetone form definite compounds with 1 mol. of acetone ("acetone of crystallisation"). In the case of α-β-diphenyl-α-naphthindole, similar compounds with ethyl methyl ketone and diethyl ketone were prepared.

### *Research Fund.*

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 9th.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences*, Vol. cxvii., No. 20, November 15, 1893.

**Determination of the True Atomic Weight of Hydrogen.**—G. Hinrichs.—The author, taking the atomic weight of oxygen as exactly = 16, calculates the value of H as 1·00025.

**The "Emetic" of Barium.**—E. Maumené.—(French chemists give the name "emetics" to a number of compounds of which the antimony-potassium tartrate is the type). M. Maumené considers that the atomic weight of tartaric acid ought to be raised. The composition of the barium "emetic" ought to be $C_8H_4O_{10},SbO_2BaO$, which would require 2·75 per cent BaO. The analyses of Dumas and Piria do not agree with this formula.

**Production of Saccharose during the Germination of Barley.**—L. Lindet.—The extracts obtained by the author contain, along with saccharose, reductive sugars, the quantity of which increases in a regular manner from the beginning to the end of germination from 2·72 to 6·28 per cent calculated on the barley. The only substance which decreases progressively during the germination of barley is starch. We cannot but be struck with the relation between the decrease of the starch and the increase of the saccharose. We have here a confirmation of the view of Brown and Morris that under certain circumstances saccharose is produced at the expense of starch.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 4.

**Top-pieces for Distillation.**—MM. Greiner and Friedrichs (*Zeit. Angew. Chemie*).—The details of the construction are not given.

**Blast for Blow-pipe Work.**—W. Hamlet.—From the Chemical News.

**A Test-tube for obtaining Stratified Reactions.**—E. Besemfelder (*Chemiker Zeitung*).—This paper requires the accompanying figure.

**Self-acting Apparatus for Washing Precipitates.**—Konrad Haack (Inaugural Dissertation).—This paper cannot be intelligibly reproduced without the accompanying plate.

**Preparation and Properties of Pure Iodine.**—C. Meinecke (*Chemiker Zeitung*).—This memoir will be inserted in full.

**Separation of Antimony and Arsenic.**—According to Fischer the chlorine compounds of both metals are reduced by ferrous chloride, and the arsenious chloride is volatilised by repeated distillation with 20 per cent hydrochloric acid. This method has been modified by Hufschmidt (*Zeit. Anal. Chemie*, xxiv., 255), who effects the distillation in a current of gaseous hydrochloric acid, and further by A. Classen and R. Ludwig (*Berichte*, xviii., 1112), who use ferrous sulphate or ammonio-ferrous sulphate for the reduction of the chlorides. Whilst in these methods a determination of the antimony can only be effected gravimetrically in the residue from the distillation, the antimony can also be determined volumetrically if, according to the proposal of Gooch and Danner, we effect the reduction of the chlorides with hydriodic acid. In this case the antimony, after the arsenious chloride has been distilled off, is determined according to the usual iodometric method. The excessive hydriodic acid does not interfere.

**Determination of Barium as Sulphate and Separation of the Alkaline Earths.**—F. W. Mar.—From the *American Journal of Science.*

**Separation of Strontium from Lime.**—P. E. Browning.—From the *American Journal of Science.*

**Determination of Barium in Presence of Calcium and Magnesium.**—F. W. Mar.—From the *American Journal of Science.*

**Determination of Antimony and of its State of Oxidation.**—F. A. Gooch and H. W. Gruener.—From the *American Journal of Science.*

**Colour Reactions of certain Aromatic Trioxy-compounds.**—J. Stahl (*Pharm. Centralhalle*).—Already inserted.

## MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.

—— Society of Chemical Industry, 8. "Application of Air in Motion to Chemical Industry, by H. G. Watel (Adjourned Discussion). "Note on the Copper Mines of Singhbhoom," by H. Harris. "The Product of the Action of Mercuric Chloride upon Metallic Silver," by Chapman Jones.

Wednesday, 6th.—Society of Arts, 8. "An Artist's View of Chicago and the World's Fair," by Frederic Villiers.

—— Society of Public Analysts, 8. "On the Estimation of Beef Stearine in Lard," by W. F. K. Stock. "An Improvement in Richmond's Milk Scale," by Charles E. Cassal and B. H. Gerrans. "Leffman-Beam Method of Fat Estimation in Milk," by H. Droop Richmond and L. K. Bosely. "On Vinegar," by Edward Collens.

Thursday, 7th.—Chemical, 8. Ballot for the Election of Fellows. "An Apparatus for the Estimation of Gases Dissolved in Water," by Dr. Truman. "Metallic Oxides and the Periodic Law," by R. M. Deeley.

Friday, 8th.—Physical, 5. "A Potentiometer for Alternating Currents," by J. Swinburne. "The Specific Resistance of Sea-Water," by W. H. Preece, F.R.S. "The Coefficient of Self-Induction of a Circular Current and The Magnetic Field of a Cylindrical Coil," by Prof. G. M. Minchin, M.A.

THE CHEMICAL NEWS.

Vol. LXVIII., No. 1776.

## INTERACTION OF QUINONES AND ORTHONITRANILINE AND NITROPARATOLUIDINE.*

By Dr. JAMES LEICESTER, Ph.D., F.C.S.,
Lecturer on Chemistry and Metallurgy at the Merchant Venturers' Technical School, Bristol.

(Concluded from p. 262).

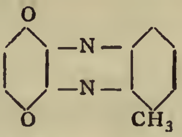
### *Quinone-α-methylphenazine.*

If mononitrotoluidoquinone be acted on under pressure with alcoholic ammonium sulphide, and the product be boiled with water, a bronze-coloured crystalline powder remains which has an exceedingly high melting-point. It dissolves in hot alcohol with a violet colour. The acetic acid solution is greenish blue, and on the addition of dilute sulphuric acid exhibits a red fluorescence.

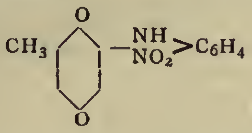
On analysis it gave the following results:—

| | Found. | Theory. |
|---|---|---|
| C .. .. | 69·2 p.c. | 69·6 p.c. |
| H .. .. | 4·2 „ | 3·6 „ |
| N .. .. | 12·8 „ | 12·5 „ |

The substance is quinone-α-methylphenazine—

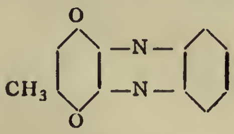


Toluquinone and *o*-nitraniline give in the same way nitranilidotoluquinone—



With alcoholic ammonium sulphide red crystals are obtained which dissolve in acetic acid with a green colour. On the addition of sulphuric acid the solution exhibits a red fluorescence.

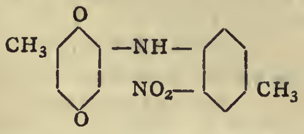
This substance is probably quinonephentolazine—



| | Found. | Theory, $C_{13}H_8N_2O_2$. |
|---|---|---|
| C .. .. | 69·2 p.c. | 69·6 p.c. |
| H .. .. | 4·4 „ | 3·6 „ |
| N .. .. | 12·9 „ | 12·5 „ |

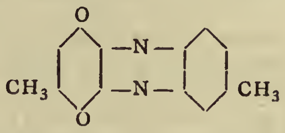
By the action of toluquinone on metanitroparatoluidine in a solution of acetic acid and alcohol crystals are obtained of a brown colour in plates which are very insoluble, and the yield is very poor.

The nitro-derivative is—



| | Found. | Theory, $C_{14}H_{12}N_2O_4$. |
|---|---|---|
| N .. .. | 10·7 p.c. | 10·3 p.c. |

The reduction product can be obtained from alcohol in red shining crystals which dissolve with a green colour in glacial acetic acid and on the addition of sulphuric acid has a weak red fluorescence and is probably a quinonetolazine—



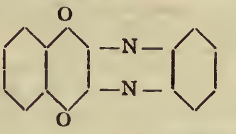
If orthonitraniline be treated with α-naphthoquinone and glacial acetic acid for four hours at 120°C. and then alcohol added straw-coloured crystals are obtained. These dissolve with an orange colour in hot alcohol and decompose at a high temperature. They yield a brilliant red-coloured powder.

| | Found. | Theory, $C_{16}H_{10}N_2O_4$. |
|---|---|---|
| N .. .. | 10·3 p.c. | 9·5 p.c. |

From this substance a reduction product of orthonitroanilidonaphthoquinone has already been obtained which fluoresces and yields a green-coloured powder crystallising from alcohol in green-coloured plates.

The acetic acid and alcoholic solutions are brown and have a green fluorescence.

This substance is probably naphthoquinonephenazine—

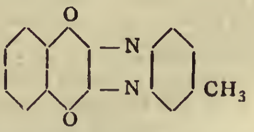


| | ound. | Theory, $C_{16}H_8N_2O_2$. |
|---|---|---|
| C .. .. | 74·4 p.c. | 73·8 p.c. |
| H .. .. | 3·9 „ | 3·1 „ |
| N .. .. | 11·1 „ | 10·7 „ |

Nitrotoluidonaphthoquinone can be prepared in the same way from metanitroparatoluidine and α-naphthoquinone in a solution of glacial acetic acid. It forms silky orange-red coloured needles. The solution in alcohol is a brownish yellow colour.

| | Found. | Theory, $C_{17}H_{12}N_2O_2$. |
|---|---|---|
| N .. .. | 9·7 p.c. | 9·1 p.c. |

The reduction product from this is α-naphthoquinonetolazine—



an olive-green coloured powder which crystallises from alcohol in steel-blue plates reflecting green light. The acetic acid and alcoholic solutions have a moss-green colour.

| | Found. | Theory, $C_{17}H_{10}N_2O_2$. |
|---|---|---|
| C .. .. | 74·4 p.c | 74·45 p.c. |
| H .. .. | 4·1 „ | 3·6 „ |
| N .. .. | 9·8 „ | 10·2 „ |

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* *Ber. d. Deutsch. Chem. Gesell.*, xxiii., 2793; *Chem. Soc. Journ.*, Abstr., 1890, 1445.

# ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 263).

A layer of gelatin 0·00004 m.m. in thickness. Aluminium and tungsten sparks. Width of slit, 0·020 m.m. Time of exposure, 1, 2 sparks; 1, 2, 4, 8, 16, 32, 96 seconds; for tungsten, three minutes. The most refrangible ultra-violet is absorbed by this extremely thin film to an unexpected degree. Even the most refrangible zinc rays appear rather enfeebled, far more than those of aluminium, and the entire portion of the tungsten spectrum beyond No. 32 is totally absent, even on exposure of several minutes. Nothing can give a better idea of the resistance which the most refrangible rays encounter, even in so thin a stratum, than the behaviour of the line No. 32. Whilst without gelatin its earliest traces appear even after exposure of one second, with gelatin it does not become visible until after four seconds. The same intensity which it acquires in eight seconds requires, if gelatin is present, three or four times the length of exposure. After an exposure of thirty-two seconds, it is more intense than after ninety-six seconds with the use of gelatin.

If we collate these results, we see that gelatin absorbs the ultra-violet up to the cadmium line No. 18 very slightly, beyond this line more strongly, but beyond the line No. 24 to such an extent that here a film of gelatin not exceeding the tenth part of the thickness of the coating of an ordinary dry plate keeps back entirely all the rays, and that even the fiftieth part of this stratum weakens the most refrangible rays (185·2) down to one-third of their original photographic energy. At the same time, we must remember that this result was obtained with gelatin plates; consequently, under the repressing influence of the same absorbent, the transparency of which has to be ascertained, how much greater would not the absorption have appeared if plates free from gelatin could have come into use?

If we wish to procure a clear conception of the resistance which gelatin opposes to the most refrangible rays in the photographic plate, we must consider more closely the relation between the thickness of the coating of the plate, the particles of silver bromide, and the gelatin films employed.

The granular silver bromide which chiefly forms the sensitive constituent of all gelatin dry plates, consists of small globular granules which, *e.g.*, in my emulsions must, according to my measurements, continued for many years, have a diameter of 0·0012 to 0·0017. These granules are very uniformly distributed in the coating of the plates. If we suppose this coating resolved into strata of the thickness of such a granule running parallel with the surface of the plate, a single stratum suffices to absorb nearly all the rays which are more strongly deflected than the line No. 24. It is here assumed only that the granules of silver bromide are not more transparent than their connecting medium—the gelatin. This assumption is so far justified, as both the mode of origination of the silver bromide in the gelatin emulsion and its general behaviour have shown that the granule is not merely embedded in the gelatin, but pervaded by it. But it appears from this exposition that the purely photochemical effect is restricted to the upper strata of the coating of the plate, and that the number of the layers decreases also with the wave length of the rays concerned. If this is the case, the relations are exactly as with plates having a very thin coating of emulsion, which always gives inexpressive pale and mostly useless proofs.

All circumstances show that the want of intensity and sensitiveness which the gelatin plate always shows in proofs of the most refrangible ultra-violet, and the sudden decrease of both beyond the cadmium line No. 24, depend to a considerable extent upon the insufficient permeability of the gelatin.

(To be continued).

# THE PREPARATION OF PURE IODINE AND SOME OF ITS PROPERTIES.

By O. MEINECKE.

Perfectly pure iodine, in which foreign constituents can no longer be detected, may be obtained by precipitating a concentrated solution of iodine in potassium iodide with water, or by precipitation with sulphuric acid from a solution containing potassium iodide and iodine. For proceeding according to the first method, a solution of potassium iodide in two parts of water is saturated with powdered iodine, and water is then added until a small portion of the iodine is deposited. After twenty-four hours it is decanted, and water again added to the clear solution. The precipitates are thoroughly washed and dried over calcium nitrate.

For the second method, a solution containing 25 grms. potassium iodate and the same weight of potassium iodide was directly precipitated with dilute sulphuric acid; the precipitate is washed until the filtrate ceases to react with sulphuric acid, and dried over sulphuric acid.

The iodine obtained according to each method is sublimed twice with, and twice without, barium oxide.

The second method yields a pure product even in presence of bromine, chlorine, and cyanogen; whilst in the first method, to avoid contamination with cyanogen, it is advantageous to add a little hydrochloric or sulphuric acid.

For working up solutions containing iodine residues (including titration residues), the author acidifies and oxidises with potassium permanganate, until brown manganese peroxide is deposited, which is separated from the iodine by decantation. After washing, it is further purified as above directed.

Further experiments of the author's relate to the purification of impure iodine. The first method, sublimation with potassium iodide, yields a pure product at once if the impurities are small. If the quantities of foreign matter are larger, the sublimation must be repeated, and the purity of the iodine obtained must always be ascertained analytically. In any case the iodine must be finally sublimed without addition.

Musset's process consists in bringing the iodide to melt in a concentrated solution of potassium iodide, from which latter product it must be separated by repeated sublimation.

Instead of the solution of potassium, Meinecke uses a solution of calcium chloride of specific gravity 1·37, adding to this liquid a few grms. of potassium iodide and a little hydrochloric acid, so that the liquid has a brown colour. The mixture is heated to the melting-point of iodine, and kept at this heat for five minutes. The iodine is washed out and sublimed once alone and once with barium oxide, when it is nearly pure. The removal of cyanogen is complete, that of bromine and chlorine less so. The quantity of the latter is so slight that a single sublimation suffices for its entire removal.

The author has made careful experiments on the hygroscopic character of iodine. Freshly sublimed iodine was placed, whilst still hot, in tightly fitting glass jars, and preserved for use over sulphuric acid. This perfectly dry preparation served both for standardising by means of sodium thiosulphate and for experiments on the moisture of portions exposed to the air, or preserved in artifically moist atmospheres. During some hours no change from absorption of moisture was perceptible, and during five days the

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

proportion of water increased only by 0·06 per cent. Even pulverised iodine, under the most favourable circumstances, takes up at most 0·1 per cent. Specimens kept for four months over sulphuric acid, and opened once or twice every week, showed no change. The author therefore recommends this method of preservation. The author, with Topf, refers the smeary condition of iodine to contamination with dust.

For determining the moisture in iodine, the author superstratifies a weighed quantity of iodine in a glass tube (which is closed with a glass stopper) with a weighed quantity of silver powder, four to five times the weight of the iodine, and weighs again. If a rise of temperature occurs, owing to the reaction of the two elements, the weighing is deferred until complete cooling. The tube is then placed in a small beaker standing on an asbestos plate, which is heated moderately, so that the formation of silver iodide takes place gradually. The upper stratum of silver must remain unchanged.

During the absorption of the iodine, the water condenses in the upper part of the tube, whence it is driven off by a stronger heat. When the tube is perfectly cold it is weighed again, when the water is found as loss.—*Zeit. f. Analytische Chemie*, xxxii., p. 462.

## BORON BRONZE.

By H. N. WARREN, Research Analyst.

THIS alloy, or more correctly speaking, aluminium-boron bronze, is brought about by the introduction of aluminium containing boron, not as aluminium boride, but existing as graphite does in cast iron. Commercially, this part of the process is accomplished by heating in a specially constructed oxyhydrogen furnace an admixture of fluorspar and vitrified boric anhydride, until the dense fumes of boron fluoride commence to appear. At this stage, ingots of aluminium are introduced into the liquid mass; reduction at once takes place with the formation of free boron, which dissolves in the aluminium, rendering it crystalline and somewhat brittle. When this so-prepared aluminium is alloyed with copper to the extent of from 5 to 10 per cent, a bronze is obtained, denser and more durable than ordinary aluminium bronze, and free from brittleness; but the most peculiar property is the perfectness with which it casts and melts; whereas, in the manufacture of aluminium bronze, one of the greatest difficulties is to ensure an uniform mixture. Often a very difficultly fusible alloy of copper and aluminium is formed upon the surface of the already melted portion, and accompanied by superficial oxidation, thus obstinately refusing to alloy with the remainder. But in the case of the boron compound no such difficulties are met with, the alloy melting perfectly, and at lower temperature than when employing pure aluminium. Boron, in fact, seems to have been little studied, but it is evidently not so serious an enemy to cope with as its halogen silicon, which, when present in minute percentages only, determines the total ruin of the bronze with which it alloys; in other words, it stands almost entirely opposite to other elements, entering into the formation, and forming compounds with the more refractory metals with the greatest ease; for instance, borides of iron, manganese, nickel, cobalt, &c., may be readily formed by the reduction of their accompanying borates in the presence of carbon, whilst those of silver, copper, gold, &c., can only be formed by the introduction of elementary boron into the fused mass; borides of the alkali metals, and even calcium, barium, &c., have also been obtained, but boride of mercury still holds out.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

Sophistication of Wax.—According to a consular report quoted in the *Chemiker Zeitung*, paraffin is extensively used in Morocco for the sophistication of bees' wax.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, November 16th, 1893.*

Dr. ARMSTRONG, President, in the Chair.

MESSRS. J. H. Coste, R. C. T. Evans, and C. A. Mitchell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. David Anderson, 14, St. Julian's Road, Kilburn, N.W.; William Edward Bamber, Spring Lawn, Heaton, Bolton; William Rowland Bird, 73, Albion Street, New Swindon, Wilts; Chuni Lal Bose, 24, Mohendro Bose's Lane, Calcutta; John Cannell Cain, Stubbins Villa, Stubbins, near Manchester; F. D. Chattaway, St. Bartholomew's Hospital, E.C.; Samuel Henry Davies, Dalton Hall, Manchester; John Duncan, M.D., St. Petersburg, Russia; Frank Evershed, Kenley, Surrey; George Trench, Standard House, Faversham; Ernest William Gay, 14, St. Julian's Road, Kilburn, N.W.; Edward Frank Harrison, 17, Bloomsbury Square, W.C.; Edmond Herbert Hills, Darland House, Chatham; John Winder Holmes, 28, Crooms Hill, Greenwich; David Hamilton Jackson, M.A., B.Sc., Royal College of Science, South Kensington; George F. Gaubert, Ph.D., Anilin Fabrik, Ludwigshafen am Rh.; Robert Leonard Jenks, 68, Victoria Road, Clapham, S.W.; A. Lapworth, 13, Duchess Road, Birmingham; Godfrey Melland, Victoria Park, Manchester; J. M. Murray, B.Sc., Highfield, Holmes Chapel, Cheshire; Richard Paulusz, Colombo; William Henry Pearson, 5, Bryn Villas, Blaina, Monmouth; J. Holms Pollock, 37, Athole Gardens, Glasgow; Meredith Young, M.B., C.M., Brighouse, Yorks.

The following is the text of a letter addressed by the President to Professor Mendeleeff, the President of the Russian Chemical Society, St. Petersburg:—

"Learning that the Society over which you preside will celebrate its 25th Anniversary on the 18th of this month, I beg, on behalf of the Chemical Society of London, to tender our most hearty congratulations and our good wishes for the future.

"Notwithstanding the grave difficulties which your language imposes, your English colleagues learn from time to time of your labours, the name of your Society and a record of its work regularly appearing in our volume of abstracts of chemical papers. We are thus frequently brought face to face with researches of the greatest interest and importance, and the wish that we could enjoy less restricted intercourse with our Russian colleagues is often felt among us. We look forward to the time when this wish will be gratified, and trust that it may not be far distant.

"Our Society is proud to have enrolled your name on its lists of foreign members, and to have welcomed you as one of its Faraday Lecturers; and the roll also includes the name of Beilstein, which, however, is no longer the mere name of an individual, but a household word throughout the chemical world, and one which cannot be mentioned without the feeling of gratitude arising in the chemist's mind. There are many other names of Russian chemists indelibly associated in our memories with discoveries of fundamental importance."

Of the following papers those marked * were read:—

*76. "*The Normal Butylic, Heptylic, and Octylic Ethereal Salts of Active Glyceric Acid.*" By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., and JOHN MACGREGOR, M.A.

The authors have previously described the preparation and properties of the methylic, ethylic, propylic, isopropylic, normal, secondary, and isobutylic salts of both inactive and active glyceric acids, and have shown that in ascending the homologous series of salts of active glyceric acid the rotatory power increases with the molecular weight, but that the rotation of the normal butylic compound is considerably less than this general relationship indicated it should be. In order to ascertain whether the increase in rotatory power continues indefinitely as the molecular weight increases, they have now prepared and examined the heptylic and octylic salts, and have also again prepared the normal butylic salt, which they had not before obtained in a state of purity. As will be seen from the subsequent Table, the results show that the rotatory power does not increase indefinitely as the homologous series is ascended, but that a maximum rotation is reached apparently at the butylic compound in the case of the normal series, the specific rotation of the heptylic being less, and that of the octylic still less than that of the normal butyl compound.

Such a maximum rotation in a homologous series has been predicted by Guye from a consideration of the successive values of the product of asymmetry, but the calculated maximum, as will be seen from the Table, falls on the propylic instead of on the butylic compound. In the case of the salts containing secondary radicles, of which, however, only the isopropylic and secondary butylic compounds have been examined, the maximum rotation is actually exhibited by the propylic compound as predicted by calculation.

| Ethereal salt. | Density, 15°/15°. | Observed rotation in 198·4 m.m. tube. $(\alpha)_D$. | Specific rotation. $[\alpha]_D$. | Molecular rotation. $[M]_D$. | Molecular deviation. $[\delta]_D$. | Product of asymmetry. $(P \times 10^6)$. |
|---|---|---|---|---|---|---|
| Methylic.. | 1·2798 | −12·2° | −4·80° | −5·76 | −27·9 | 288·8 |
| Ethylic .. | 1·1921 | 21·7 | 9·18 | 12·30 | 52·8 | 344·8 |
| Propylic .. | 1·1448 | 29·4 | 12·94 | 19·15 | 74·9 | 358·2 |
| Isopropylic | 1·1303 | 26·5 | 11·82 | 17·49 | 67·8 | 358·2 |
| Butylic (norm.) | 1·1084 | 29·0 | 13·19 | 21·37 | 77·0 | 346·8 |
| Isobutylic | 1·1051 | 31·2 | 14·23 | 23·05 | 82·9 | 346·8 |
| Butylic (sec.) | 1·1052 | 23·2 | 10·58 | 17·14 | 61·7 | 346·8 |
| Heptylic.. | 1·0390 | 23·3 | 11·30 | 23·05 | 68·3 | 268·7 |
| Octylic .. | 1·0263 | 20·8 | 10·22 | 22·28 | 62·6 | 241·8 |

*77. "*The Ethereal Salts of Diacetylglyceric Acid in Relation to the Connection between Optical Activity and Chemical Constitution.*" By Percy Frankland, Ph.D., B.Sc., F.R.S., and John MacGregor, M.A.

The methylic, ethylic, propylic, isopropylic, and isobutylic salts of active diacetylglyceric acid were prepared by heating the corresponding salts of active glyceric acid with an excess of acetyl chloride, and then fractionally distilling *in vacuo*. These compounds are colourless, almost inodorous liquids, volatilising without decomposition even under ordinary atmospheric pressure at between 200° and 300°. The special interest attaching to them consists in the circumstance that, both in the methylic and ethylic compounds respectively, two of the groups attached to the asymmetric carbon atom are of equal mass, and, therefore, according to Guye's theory, these two compounds should be inactive, or nearly so, or at any rate some of the members of this series should exhibit a rotation of opposite sign to that exhibited by the glycerates. As will be seen from the Table, some of these anticipations are realised, the sign throughout being similar to that of the ethereal salts of glyceric acid, the increase in rotation on ascending the series of diacetylglycerates proceeding on lines almost parallel to those followed in ascending the glycerate series, the diacetylglycerates only starting from a higher level of rotation, so to speak. The authors consequently again urge the necessity of also taking into consideration the qualitative nature of the groups attached to the asymmetric carbon atom, and not their masses only.

| Ethereal salt. | Density, 15°/15°. | Observed rotation at 15° C. in 198·4 m.m. tube. $(\alpha)_D$. | Specific rotation. $[\alpha]_D$. | Molecular rotation. $[M]_D$. | Molecular deviation. $[\delta]_D$. | Products of asymmetry. $(P \times 10^6)$. |
|---|---|---|---|---|---|---|
| Methylic.. | 1·1998 | −28·65° | −12·04° | −24·56° | −80·0 | 0·0 |
| Ethylic .. | 1·1574 | 37·46 | 16·31 | 35·56 | 108·2 | 0·0 |
| Propylic .. | 1·1263 | 43·52 | 19·47 | 45·17 | 129·5 | 17·4 |
| Isopropylic | 1·1193 | 39·90 | 17·97 | 41·69 | 119·1 | 17·4 |
| Isobutylic | 1·0990 | 44·66 | 20·48 | 50·38 | 136·7 | 41·9 |

### Discussion.

Mr. L. M. Jones observed that inasmuch as the product of dissymmetry employed presupposes the equality of the distances of the centres of gravity of the combined groups from the central carbon atom, it can only give an approximate indication of where the maximum "molecular deviations" will be found. In the case of the diacetylglycerates, as the salts which have this product = 0 show marked activity, we should expect considerable divergence between the observed and predicted maxima.

Mr. Rodger drew special attention to the fact that the "molecular deviation,"—

$$\frac{a}{l} \times \sqrt[3]{\frac{M}{d}},$$

employed by Guye in a recent communication, was probably the true value of the molecular rotatory power. $\frac{a}{l}$ is evidently the angle of rotation produced by unit length of substance.

$$\sqrt[3]{\frac{M}{d}}$$

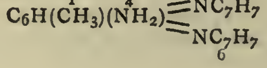
is the molecular length or a length which for different substances contains the same number of molecules, and the "molecular deviation" is, therefore, proportional to the angle of rotation produced by the same number of molecules or to the rotation per molecule. The dimensions of this quantity are those of an angle,—the physical magnitude actually measured,—whereas the ordinary measure of molecular rotation,—

$$\frac{a}{l} \times \frac{M}{d},$$

is an angle multiplied by a surface. He also pointed out that the effect of temperature on rotatory power had been little studied. Such experiments as had been made indicated, however, that the temperature change varied with the chemical nature of the substance, and hence that relationships obtained at the same temperature, according to the usual custom, would no longer be the same if the temperature of comparison were altered. For these reasons the significant speculations of Guye could only be subjected to a fair test when "molecular deviations" had been measured at temperatures at which, as regards the property under consideration, the substances were in comparable states.

*78. "*The Oxidation of Paratoluidine.*" By Arthur G. Green.

The red crystalline substance obtained by Barsilowsky in 1873 by oxidising paratoluidine with potassium ferrocyanide has been variously considered as a polymeric parazotoluene, as a tritoluylene-diamine, and a complex amidoazo-compound. The author has re-examined this remarkable substance. He arrives at the conclusion that the substance is a diparatolylimide represented by the formula—



$$C_6H(\overset{1}{C}H_3)(\overset{4}{N}H_2)\begin{cases}=N\overset{3}{C}_7H_7\\=N\underset{6}{C}_7H_7\end{cases}$$

derived from amidotoluquinone. This conclusion is deduced from the following facts. The base has the empirical composition $C_7H_7N$, and its molecular weight corresponds to the formula $C_{21}H_{21}N_3$. By treatment with chlorhydric acid it is readily decomposed, one paratoluidine residue being split off and a second being removed by further treatment of the intermediate product. On reduction, it takes up 2 atoms of hydrogen, affording a stable, colourless leuco-base. This latter is readily reoxidised to the original substance, has very slight basic properties, and is not decomposed by acids or further reduced by boiling with stannous chloride. The leuco-base condenses readily with benzil, forming a coloured azonium compound; and it yields colourless, non-oxidisable anhydro-compounds with formic and acetic acids, thus showing all the characteristics of a mono-substituted orthodiamine. This result, taken in conjunction with the presence of two paratolylimide groups in the original substance, as shown by its decomposition by acids, proves that the leuco-base is a diparatolyltriamidotoluene. Of the three possible formulæ for this compound the greatest probability attaches to that in which the two tolylamido-groups are relatively in the para-position. This formula would represent the leuco-base as an amido-derivative of diparatolylparatolylenediamine. The diparatolylparatolylenediamine was accordingly prepared by heating hydrotoluquinone with paratoluidine and zinc chloride and submitted to comparison with the leuco-base. A marked similarity in appearance and properties was observable, entirely in accordance with the view that the latter is the amido-derivative of the former. Moreover, the diparatolylparatolylenediamine was converted by oxidation into toluquinonediparatolyldiamine, and this substance showed a striking similarity in its appearance and in all its properties to Barsilowsky's base. There could, therefore, be little doubt that the tolylamido-groups in the leuco-base and the tolyl-imido-groups in the original compound occupy the para-position to each other, and that consequently the constitution of the Barsilowsky base is that given above, whilst its leuco-compound must be represented by the formula—

$$C_6H_2(CH_3)(NH_2)(NHC_7H_7)\ [1:4:3:6].$$

In agreement with this conclusion, the synthesis of Barsilowsky's base was effected by oxidation of a mixture of orthamidometaparaditolylamine and paratoluidine in acetic acid solution, whilst its lower homologue was prepared in a similar manner from orthamidometaparaditolylamine and aniline.

*79. "*The Action of Benzoic Chloride on Urine in presence of Alkali. Formation of Benzoic Derivatives of Urochrome.*" By J. L. W. Thudichum, M.D., F.R.C.P.

The author has examined the products of the action of benzoic chloride on urine in the presence of alkali. The urine rendered strongly alkaline with soda, and filtered from the precipitated phosphates, is mixed with benzoic chloride in the proportion of 50 c.c. for each litre of urine used. The mixture is kept cool and constantly agitated, care being taken to maintain a strong alkaline reaction. A yellowish white, semi-solid precipitate separates, which by extraction with alcohol may be separated into three parts: (1) an oily substance soluble in cold alcohol, (2) a solid soluble in hot alcohol, (3) a small quantity of a solid insoluble in boiling alcohol, which was not further examined. The oil and the solid substances are considered to be mixtures of various benzoic derivatives of *urochrome*, the normal colouring matter of urine, and of alcoholic compounds present in the urine. The mixed solid derivatives of urochrome contain between 58·9 and 63·2 per cent of carbon, 5 per cent of hydrogen, and between 3 and 1·5 per cent of nitrogen, from which the author concludes that they are mixtures of polybenzoic derivatives, as he found 12 per cent of nitrogen in urochrome.

The solid benzoic derivatives may be most readily crystallised by dissolving the original precipitate in boiling absolute alcohol, filtering the hot liquid, and evaporating until crystallisation begins. By fractionally crystallising the resulting mass from hot alcohol, the author separated it into three portions: (1) a crystalline solid not dissolved by boiling spirit ("insoluble ester"), (2) crystalline needles soluble in boiling spirit ("needle ester"), (3) laminæ resembling cholesterol in appearance soluble in cold spirit ("cholesteroid ester"). The mother-liquor contains for the most part the oily benzoic derivatives of urochrome.

By the action of benzoic chloride on an aqueous solution of urochrome (prepared by the ferric chloride method), solid benzoic derivatives were obtained containing 1·77 per cent of nitrogen. The same result may be secured by precipitating urine with phosphotungstic acid, regenerating by means of baryta, and extracting the residue with alcohol. The alcoholic solution, when mixed with mercuric chloride, furnishes a precipitate containing the urochrome and other bases. If this precipitate be decomposed with hydrogen sulphide, an acid liquid is obtained which, when acted on with benzoic chloride and soda, affords a precipitate of the benzoic derivatives of urochrome. Similarly, if the precipitate obtained by adding phosphotungstic or phosphomolybdic acid to acidified urine be dissolved in soda and the solution be mixed with benzoic chloride, the same derivatives of urochrome are precipitated. From this behaviour the author concludes that urochrome is at once an alcohol and a base.

The benzoic derivatives of urochrome are hydrolysed by strong alkali, but the liberated urochrome is, to some extent, decomposed, especially if the liquid be heated. Some, however, may be recovered by acidulating the strong alkaline solution with dilute sulphuric acid and precipitating with phosphotungstic acid and decomposing the precipitate with barium carbonate in the usual manner. When the derivatives are hydrolysed by heating with dilute sulphuric acid, much of the liberated urochrome suffers decomposition, producing the substance called by the author *uropittin*, as well as other urochrome "resins" (*uromelanin* and *omicholin*). Neither urochrome nor its black decomposition product, uromelanin, are carbohydrates. Both contain nitrogen.

The "cholesteroid" benzoic derivative obtained from urine furnished on combustion results agreeing with the formula $C_{13}H_{12}O_8$. When hydrolysed with dilute sulphuric acid, it yields about 50 per cent of benzoic acid, together with a resinous substance. It contained only a trace of nitrogen, and is probably the derivative of an alcohol. The author obtained no benzoic derivative of any substance in the nature of a sugar (*cf.* Wedenski, *Zeit. physiol. Chem.*, xiii., 122).

80. "*The Combination of Hydrocarbons with Picric Acid and other Nitro-compounds.*" By William A. Tilden and Martin O. Forster.

The authors have instituted a compound described by Lextrait in 1886, which is formed by heating picric acid with pinene. It contains the elements of picric acid and a terpene, but differs from the picrates of other hydrocarbons in forming a peculiar potassium salt, in yielding picramide and borneol when submitted to the action of alcoholic ammonia, and in forming borneol and not simply a hydrocarbon under the influence of aqueous alkalis.

The authors have also instituted experiments on the behaviour of other hydrocarbons with nitro-compounds generally, from which it appears that, in order that a compound may be formed, at least *two* nitro-groups must be present in the nitro-derivative concerned. They conclude that the oxygen of the nitro-groups affords the link which, in ordinary cases, binds the hydrocarbon to the nitro-compound, while in the case of the pinene derivative the oxygen of the hydroxyl is probably also involved.

81. "*The Formation of Pyrrol Derivatives from Aconitic Acid.*" By S. Ruhemann, Ph.D., M.A., and F. E. Allhusen, B.A.

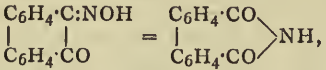
The authors find that when the ethereal salt of dibromotricarballylic acid (which they prepared by exposure of a mixture of ethylic aconitate and bromine to direct sunlight) and aniline interact, besides a compound melting at 87—88°, which they regard as ethylic anhydroanilaconitate, an oil is formed which, on heating at 250—260°, yields an isomeride, ethylic phenylpyrrolonedicarboxylate, melting at 181°.

82. "*The Conversion of α-Hydrindonoxime into Hydrocarbostyril.*" By F. Stanley Kipping, Ph.D., D.Sc.

The peculiar intramolecular change first observed by Beckmann in the case of diphenylacetoxime has been carefully studied by V. Meyer, Hantsch, and others during the last few years, and it has been shown that a great many open-chain hydroximes may be converted into substituted amides in accordance with the equation—

$$RR'C:NOH = R{\cdot}CO{\cdot}NH{\cdot}R' \text{ or } R{\cdot}NH{\cdot}CO{\cdot}R'.$$

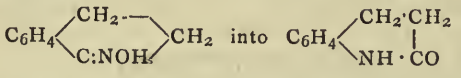
The behaviour of hydroximes of cycloid ketones, however, has been but little investigated. Camphoroxime has been shown to yield campholenonitrile, $C_{10}H_{15}N$, and not a substituted amide, as was to be expected from the behaviour of isonitrosocamphor, which yields camphorimide (Angelo, *Ber.*, xxvi., 59; Manasse, *ibid.*, 241), and the only case, in fact, in which the desired change has hitherto been accomplished with the hydroxime of a cycloid ketone of known constitution appears to be that of phenanthraquinonemonoxime, which as Wegerhoff has shown (*Ber.*, 1888, 2355), is readily transformed into diphenimide—



the closed chain of 6 carbon atoms being converted into a closed chain of 7 atoms by the introduction of an imido-group.

These considerations led the author to study the behaviour of hydrindonoxime. On subjecting this to the action of phosphorus pentachloride and water successively, it yielded a small quantity of a crystalline substance melting at 163°, represented by the formula $C_9H_9NO$ (found C = 73·26; H = 6·32; required C = 73·47; H = 6·12 per cent). As far as could be ascertained without direct comparison, this substance is identical with hydrocarbostyril.

This change from—



is, to some extent, analogous to the conversion of pyrroline into chloro- or bromo-pyridine, which appears to be one of the few cases on record of the conversion of a ring with 5 into one containing 6 elements, although the reverse operation, namely, the transformation of a ring containing 6 into one containing 5 elements is known, from Zincke's work, to be easily accomplished.

The publication of this note is desirable owing to the appearance of a paper by Wallach in the last number of the *Annalen* (cclxxvii., 154), in which he describes preliminary experiments on the behaviour of hydroximes of cycloid ketones.

83. "*The Constitution of Lapachol and its Derivatives. II. The Azines of the Lapachol Group.* By Samuel C. Hooker.

The author gives an account of azines of the lapachol group prepared from orthotolylenediamine, and fully discusses the relations existing between lapachol and α- and β-lapachone and the changes occurring in the quinone group in the course of the transformation of these compounds into each other. The constitution of several of the compounds is discussed in relation to their colour. The compounds described are methyllapazine, methylbromolapazine, methyllapeurhodone, methylhydroxylapeurhodone, methyl-α-naphtheurhodol, and methylchloronaphtheurhodone.

## PHYSICAL SOCIETY.

*Ordinary Meeting, November 24th, 1893.*

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Col. Maitland, C.B., was elected a member of the Society.

Prof. S. P. Thompson then occupied the chair,

Whilst the President read a paper "*On the Magnetic Shielding of Concentric Spherical Shells.*"

In this mathematical investigation the author considers cases in which the equipotential surfaces are surfaces of revolution about a line through the centre of the shells, and the permeability ($\mu$) of each shell is constant. Taking the common centre as origin, the potential within any shell is expanded in terms of zonal spherical harmonics, and the ratio of the shielded to the unshielded field determined. The following important result is arrived at, viz., if the permeabilities of the enclosed and external space be the same, then the ratios of the shielded to the unshielded fields are the same *for each harmonic term*, whether the part shielded be external or internal. It is also shown that the shielding effect on external space when a small magnet is placed at the centre of the shell is the same as the shielding effect on the enclosed space when the shells are placed in an uniform magnetic field.

The case of a single shell with a small magnet at the centre is next considered, where the permeabilities of the internal and external spaces are taken as unity. Here the shielding depends on the ratio of the outer to the inner radius ($a_1/a_0$). When the thickness of the shell is 1/100 of $a$, the ratio of shielded to unshielded field ($\Psi/\psi_0$) is 3/13 when $\mu = 500$, and 3/23 when $\mu = 1000$.

For $\mu = 1000$, increasing the thickness from $a_1/10$ to $a_1/2$ changes the shielding from 1/60 to 1/194, thus showing that after the shell is moderately thick, further increasing the thickness is not very effective. When the small magnet is displaced from the centre of the shell with its axis along a radius, then the shielding effect of the shell is greater on the side towards which the magnet is moved, and less on the opposite side. Thickening a single shell being inefficient, the effect of using two or three shells separated by air gaps is investigated. Here, as in the case of a single shell, the shielding is improved by adding permeable material either within the inner or without the outer shell. If the inner and outer diameters are given then, when the difference in these diameters is small one continuous shell gives the best result. For a larger difference two shells separated by an air gap are much more efficient than a single one, and filling up the air gap would appreciably diminish the screening effect. When the permeability of the substance is high, the best shielding is obtained when the radii of the bounding surfaces of the shells are in geometrical progression. The great value of lamination is shown in the following Table, where the volume of the permeable material is expressed in terms of that of the enclosed space, and the shielding in each case being the best:—

| | Volume of material used. | External field. |
|---|---|---|
| Single shell.. .. .. | 1·0 | 0·018 |
| Two shells .. .. .. | 5·0 | 0·0006 |
| Three ,, .. .. .. | 4·8 | 0·00016 |
| Single shell.. .. .. | 7·0 | 0·0102 |

The conditions for the best arrangement in each of the following cases are fully worked out in the paper, viz.:— Two shells when the largest and smallest radii and the volume of the material used are given; two contiguous shells of different permeabilities; and three shells of different permeabilities.

The main results of the investigation are that with thin shells lamination is useless, whilst with thick shells it is essential if the best effect is desired. Experiments made on actual shells had fully confirmed the theoretical conclusions.

Prof. **Minchin** said the mathematical results were very simply expressed. Although the work was apparently restricted to zonal spherical harmonics, some of the important formulæ apply equally to general spherical harmonics. Referring to the difficulty of shielding by single thick shells, he pointed out that the equation giving the relation between the shielded and the unshielded fields with different thicknesses of shell represented a hyperbola with its asymptotes parallel to the axes; hence the shielding tended to a definite limit as the thickness increased indefinitely.

Mr. **Evershed** said he had been engaged for the last two years on the subject of magnetic shielding with a view to screening measuring instruments from external fields. In such cases it was not possible to use closed shells, and this introduced trouble. The best result he had yet obtained was to reduce the disturbance to about one-fifth. Another difficulty was introduced by the fact of the shield being magnetised by the current passing through the coil, and owing to hysteresis, the permeability was different according as the magnetisation increased or decreased. By using an outer iron shell a great improvement had been effected. To obtain the best results it was important to have no joints in the shields. A coil frame with two shields of bent iron was exhibited.

Mr. J. **Swinburne** remarked that the subject divided itself into two: shielding instruments and shielding sources. If a dynamo itself be shielded, this did not prevent the currents in the leads producing magnetic disturbances. This was very important in ships. By using an alternator with revolving fields all disturbances could be avoided.

Dr. C. B. **Burton** enquired whether by considering the hydro-dynamical analogue of a porous material the case of perforated shells could be elucidated?

Mr. A. P. **Trotter** wished to know if the homogeneity of the shield was of much consequence? At Oxford it had been found that a screen of four inches of scrap iron was better than boiler plate.

Mr. **Blakesley** asked if the effect of moving a magnet sideways in a sphere had been observed? He thought the mathematics developed in the paper would be useful in working out the magnetic theory of the earth.

Prof. S. P. **Thompson** thought that taking the permeability as constant would not be quite correct, for $\mu$ was a function of the magnetisation. Hence in the cases considered the outer shell would be the more permeable.

In his reply the **President** said scrap iron in contact was not like clear space, for there were comparatively free paths for the induction at the points of contact. As regards the shielding of the dynamo at Greenwich, Mr. Christie had written to say that the credit was due to the makers of the machine and shields, Messrs. Johnson and Phillips.

Prof. G. M. **Minchin**, M.A., read a paper on "*The Action of Electromagnetic Radiation on Films containing Metallic Powders.*"

After noticing the resemblance of the phenomena exhibited by tubes containing metallic filings shown by Mr. Croft on October 27 to those of photoelectric impulsion cells, he repeated some of the experiments with filings, and found the effects when the filings were of ordinary fineness. He also noticed that the experiments did not succeed either when the filings were very coarse or very fine. Coarse ones always conducted, whilst very fine filings or powders acted as insulators, except when strongly compressed. To establish a closer connection with the impulsion cells, he tried films of gelatin or collodion containing metallic powders. Directions for preparing the films are given in the paper. On inserting such a film in circuit with a battery, key, and galvanometer, it acts as an insulator. To render a small portion conducting, the electrodes on the surface of the film are brought very close together, and one of the wires touched with an electrified body (an electric gas lighter was often used). This caused a current to pass. The electrodes may then be separated a little further, and the process repeated until any desired portion is rendered conducting. The peculiarity of such a film is that if the circuit be broken at the film, the film becomes an insulator; whereas, breaking the circuit at any other point leaves the film conducting. The action of the spark or charges on the conductivity of the films is attributed to the influence of electric surgings produced in the wires by the electric discharges.

The **President** read a written communication from Prof O. J. Lodge, in which the writer suggested that the phenomena of the films, and also of Lord Rayleigh's water-jet experiment (in which water drops are caused to coalesce by the presence of an electrified body), were due to the range of molecular attraction being increased by electric polarisation.

Mr. **Blakesley** said he had tried Mr. Croft's experiments, and found that conductivity could be established in a tube of filings whilst the circuit was inclosed. Breaking the circuit of a transformer or electromagnet would produce conductivity; hence he concluded that electric surgings were not essential. Another curious experiment was to put the discharging knobs of an electric machine on a photographic plate at a distance of a few inches. On turning the machine a small spark travels slowly along the plate from the negative to the positive knob. On reversing the polarity of the machine, the spark travels back along the same path, but if the polarity remains unchanged, a second spark usually travels along a different path.

Prof. C. V. **Boys** asked Prof. Minchin whether the films themselves, or the contacts between the electrode and film, is made conducting by the sparks?

Prof. S. P. **Thompson** wished to know if ordinary photographic dry plates would serve the purpose?

Mr. **Evershed** enquired whether the metal used as electrode made any difference?

Prof. **Minchin**, in his reply, maintained that the phenomena were due to electric impulses. He had not tried photographic plates, and had always used platinum for his electrodes.

## THE ROYAL SOCIETY.

*Anniversary Meeting, November 30th, 1893.*

### *Address of the President*, Lord Kelvin, D.C.L., LL.D.

Since our last Anniversary Meeting, the Royal Society has lost eleven Fellows on the Home List, and two Foreign Members.

Henry Tibbats Stainton, December 2, 1892, aged 70.
Sir Richard Owen, December 18, 1892, aged 89.
Dr. James Jago, January 18, 1893, aged 77.
Henry Francis Blanford, January 23, 1893, aged 58.
Thomas William Fletcher, February 1, 1893, aged 84.
Edward Walker, March 2, 1893, aged 73.
Alphonse de Candolle, March 28, 1893, aged 87.
Henry Edward Stanley, Earl of Derby, April 21, 1893, aged 67.
Ernest Edward Kummer, May 14, 1893, aged 84.
Rev. Charles Pritchard, May 28, 1893, aged 85.
Dr. John Rae, July 22, 1893, aged 80.
Thomas Hawksley, September 23, 1893, aged 86.
Sir Andrew Clark, Bart., November 6, 1893, aged 67.

Biographical notices will be found in the *Proceedings*.

During the past session our standing committees have been as active as ever. The Library Committee have again had before them the question of finding accommodation to meet the rapid growth of our Library. One measure which, with the consent of the Council, they have adopted to this end has been to part with a number of the literary and philosophical series of transactions published by those societies which are not, like our own, purely scientific. In some cases these series are being returned to the institutions who gave them; in others, where this is not desired, they are presented to libraries in which they will be of greater use than in our own.

The House and Soirée Committee have held more than their usual number of meetings; and, acting upon their advice, the Council appointed a Special Committee to arrange for the better accommodation of the Fellows at their ordinary meetings and of their visitors at the Annual Soirées. Upon the first floor a new doorway has been provided, which, it is hoped, will help to a freer circulation on the crowded nights of our Soirées, and on the ground floor, besides the arrangement of the meeting-room and the provision of a lecture table, and additional accommodation for diagrams, a preparation room is being fitted with suitable appliances for the use of those who are willing to illustrate their papers by experiment.

The generous gift of £2000 presented by our Fellow Mr. Ludwig Mond, in the early part of the session, to aid the work of the "Catalogue of Scientific Papers," has enabled the Catalogue Committee not only to carry on the current work of the Catalogue, which want of funds threatened to cripple, but also to take into consideration wider schemes than it was possible to contemplate before. The Committee have met several times during the past session, and it is hoped that the long-desired Subject Index may yet become an accomplished fact.

The Water Research Committee have continued their labours, and a Second Report on the vitality of microscopic pathogenic organisms in large bodies of water, dealing with the vitality and virulence of *Bacillus anthracis* and its spores, the result of Messrs. Percy Frankland and Marshall Ward's researches, has been completed during the past session and published in our *Proceedings*.

Except that additional assistants have been employed in the Catalogue Department, our staff remains unchanged.

During the past year, in the Mathematical and Physical Section of the *Philosophical Transactions*, twenty-one papers have been published, and in the Biological Section, ten; the two sections together containing a total of 1775 pages of letter-press, and 70 plates. Of the *Proceedings*, twelve numbers have been issued, containing 1282 pages and 19 plates.

Not the least important of the scientific events of the year is the publication, in the original German and in an English translation by Professor D. E. Jones, of a collection of Hertz's papers describing the researches by which he was led up to the experimental demonstration of magnetic waves. For this work the Rumford Medal of the Royal Society was delivered to Professor Hertz three years ago by my predecessor, Sir George Stokes. To fully appreciate the book now given to the world, we must carry our minds back to the early days of the Royal Society, when Newton's ideas regarding the forces which he saw to be implied in Kepler's laws of the motions of the Planets and of the Moon were frequent subjects of discussion at its regular meetings and at perhaps even more important non-official conferences among its Fellows.

In 1684 the Senior Secretary of the Royal Society, Dr. Halley, went to Cambridge to consult Mr. Newton on the subject of the production of the elliptic motion of the Planets by a central force,* and on the 10th of December of that year he announced to the Royal Society that he "had seen Mr. Newton's book, 'De Motu Corporum.'" Some time later, Halley was requested to "remind Mr. Newton of his promise to enter an account of his discoveries in the register of the Society," with the result that the great work "Philosophiæ Naturalis Principia Mathematica" was dedicated to the Royal Society, was actually presented in manuscript, and was communicated at an ordinary meeting of the Society on the 28th of April, 1686, by Dr. Vincent. In acknowledgment, it was ordered "that a letter of thanks be written to Mr. Newton, and that the printing of his book be referred to the consideration of the Council; and that in the meantime the book be put into the hands of Mr. Halley, to make a report thereof to the Council." On the 19th of May following, the Society resolved that "Mr. Newton's 'Philosophiæ Naturalis Principia Mathematica' be printed forthwith in quarto, in a fair letter; and that a letter be written to him to signify the Society's resolution, and to desire his opinion as to the volume, cuts, &c." An exceedingly interesting letter was accordingly written to Newton by Halley, dated London, May 22, 1686, which we find printed in full in Weld's "History of the Royal Society" (vol. i., pp. 308—309). But the Council knew more than the Royal Society at large of its power to do what it wished to do. Biology was much to the front then, as now, and the publication of Willughby's book, "De Historia Piscium," had exhausted the Society's finances to such an extent that the salaries even of its officers were in arrears. Accordingly, at the Council meeting of the 2nd of June, it was ordered that "Mr. Newton's book be printed, and that Mr. Halley undertake the business of looking after it, and printing it at his own charge, which he engaged to do."

It seems that at that time the office of Treasurer must have been in abeyance; but with such a Senior Secretary as Dr. Halley there was no need for a Treasurer.

Halley, having accepted copies of Willughby's book, which had been offered to him in lieu of payment of arrears of salary* due to him, cheerfully undertook the printing of the "Principia" at his own expense, and entered instantly on the duty of editing it with admirable zeal and energy, involving, as it did, expostulations, arguments, and entreaties to Newton not to cut out large parts of the work which he wished to suppress† as being too slight and popular, and as being possibly liable to provoke questions of priority. It was well said by Rigaud, in his "Essay on the first publication of the Principia," that "under the circumstances, it is hardly possible to form a sufficient estimate of the immense obligation which the world owes in this respect to Halley, without whose great zeal, able management, unwearied perseverance, scientific attainments, and disinterested generosity the 'Principia' might never have been published."‡ Those who know how much worse than "law's delays" are the troubles, cares, and labour involved in bringing through the press a book on any scientific subject at the present day will admire Halley's success in getting the "Principia" published within about a year after the task was committed to him by the Royal Society, two hundred years ago.

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* Whewell's "History of the Inductive Sciences," vol. ii., p. 77.

* It is recorded in the Minutes of Council that the arrears of salary due to Hooke and Halley were resolved to be paid by copies of Willughby's work. Halley appears to have assented to this unusual proposition, but Hooke wisely "desired six months' time to consider of the acceptance of such payment."

The publication of the "Historia Piscium," in an edition of 500 copies, cost the Society £400. It is worthy of remark, as illustrative of the small sale which scientific books met with in England at this period, that, a considerable time after the publication of Willughby's work, Halley was ordered by the Council to endeavour to effect a sale of several copies with a bookseller at Amsterdam, as appears in a letter from Halley requesting Boyle, then at Rotterdam, to do all in his power to give publicity to the book. When the Society resolved on Halley's undertaking to measure a degree of the Earth, it was voted that "he be given £50 or fifty 'Books of Fishes'" (Weld's "History of the Royal Society," vol. i., p. 310).

† "The third [book] I now design to suppress. Philosophy is such an impertinently litigious lady that a man bad as good be engaged in lawsuits as have to do with her. I found it so formerly, and now I am no sooner come near her again but she gives me warning. The first two books without the third will not so well bear the title of 'Philosophiæ Naturalis Principia Mathematica,' and therefore I have altered it to this, 'De Motu Corporum Libri duo'; but, upon second thoughts, I retain the former title. 'Twill help the sale of the book, which I ought not to diminish now 'tis yours" (*Ibid.* p. 311).

‡ *Ibid.*, p. 310.

When Newton's theory of universal gravitation was thus made known to the world Descartes's *Vortices*, an invention supposed to be a considerable improvement on the older invention of crystal cycles and epi-cycles from which it was evolved, was generally accepted, and seems to have been regarded as quite satisfactory by nearly all the philosophers of the day.

The idea that the Sun pulls Jupiter, and Jupiter pulls back against the Sun with equal force, and that the Sun, Earth, Moon, and Planets all act on one another with mutual attractions, seemed to violate the supposed philosophic principle that matter cannot act where it is not. Descartes's doctrine died hard among the mathematicians and philosophers of Continental Europe; and for the first quarter of last century belief in universal gravitation was an insularity of our countrymen.

Voltaire, during a visit which he made to England in 1727, wrote:—"A Frenchman who arrives in London finds a great alteration in philosophy, as in other things. He left the world full; he finds it empty. At Paris you see the universe composed of vortices of subtle matter; at London we see nothing of the kind. With you it is the pressure of the Moon which causes the tides of the sea; in England it is the sea which gravitates towards the Moon. . . . You will observe also that the Sun, which in France has nothing to do with the business, here comes in for a quarter of it. Among you Cartesians all is done by impulsion: with the Newtonians it is done by an attraction of which we know the cause no better."[*] Indeed, the Newtonian opinions had scarcely any disciples in France till Voltaire asserted their claims on his return from England in 1728. Till then, as he himself says, there were not twenty Newtonians out of England.[†]

In the second quarter of the century sentiment and opinion in France, Germany, Switzerland, and Italy experienced a great change. The mathematical prize questions proposed by the French Academy naturally brought the two sets of opinions into conflict. A Cartesian memoir of John Bernoulli was the one which gained the prize in 1730. It not unfrequently happened that the Academy, as if desirous to show its impartiality, divided the price between Cartesians and Newtonians. Thus, in 1734, the question being the cause of the inclination of the orbits of the planets, the prize was shared between John Bernoulli, whose memoir was founded on the system of vortices, and his son Daniel, who was a Newtonian. The last act of homage of this kind to the Cartesian system was performed in 1740, when the prize on the question of the tides was distributed between Daniel Bernoulli, Euler, Maclaurin, and Cavallieri; the last of whom had tried to amend and patch up the Cartesian hypothesis on this subject.[‡]

On the 4th of February, 1744, Daniel Bernoulli wrote as follows to Euler:—"Uebrigens glaube ich, dass der Aether sowohl *gravis versus solem*, als die Luft versus terram sey, und kann Ihnen night bergen, dass ich über diese Puncte ein völliger Newtonianer bin, vnd verwundere ich mich, dass sie den Principiis Cartesianis so lang adhäriren; es möchte wohl einige Passion vielleicht mit unterlaufen. Hatt Gott können eine *animam*, deren Natur uns unbegreiflich ist, erchaffen, so hat er auch können eine attractionem universalem materiae imprimiren, wen gleich solche attractio *supra captum* ist, da hingegen die Principia Cartesiana allzeit *contra captum* etwas involviren."

Here the writer expressing wonder that Euler had so long adhered to the Cartesian principles, declares himself a thorough-going Newtonian, not merely in respect to gravitation *versus* vortices, but in believing that matter may have been created simply with the law of universal attraction without the aid of any gravific medium or mechanism. But in this he was more Newtonian than Newton himself.

Indeed Newton was not a Newtonian, according to Daniel Bernoulli's idea of Newtonianism, for in his letter to Bentley of date 25th February, 1692,[*] he wrote:—"That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance through a vacuum without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it." Thus Newton, in giving out his great law, did not abandon the idea that matter cannot act where it is not. In respect, however, merely of philosophic thought, we must feel that Daniel Bernoulli was right; we can conceive the Sun attracting Jupiter, and Jupiter attracting the Sun, without any intermediate medium, if they are ordered to do so. But the question remains—Are they so ordered? Nevertheless, I believe all, or nearly all, his scientific contemporaries agreed with Daniel Bernoulli in answering this question affirmatively. Very soon after the middle of the Eighteenth Century, Father Boscovich[†] gave his brilliant doctrine (if infinitely improbable theory) that elastic ridigity of solids, the elasticity of compressible liquids and gases, the attractions of chemical affinity and cohesion, the forces of electricity and magnetism—in short, all the properties of matter except heat, which he attributed to a sulphureous fermenting essence—are to be explained by mutual attractions and repulsions, varying solely with distances, between mathematical points endowed also, each of them, with inertia. Before the end of the Eighteenth Century the idea of action-at-a distance through absolute vacuum had become so firmly established, and Boscovich's theory so unqualifiedly accepted as a reality, that the idea of gravitational force or electric force or magnetic force being propagated through and by a medium seemed as wild to the naturalists and mathematicians of one hundred years ago as action at-a-distance had seemed to Newton and his contemporaries one hundred years earlier. But a retrogression from the Eighteenth Century school of science set in early in the Nineteenth Century.

(To be continued).

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Determination of the Acid Hydrazides.—H. Strache and S. Tritzer (*Monatshefte fur Chemie*).—The authors have experimented on compounds of the general formula $RNH—NHC_6H_5$, where R signifies a univalent acid radicle. The authors prove that the acid hydrazides are oxidised by boiling Fehling's solution in the same manner as phenylhydrazine, with liberation of the total nitrogen.

Examination of Tartaric Acid and Citric Acid for Metallic Lead and Compounds of Lead.—M. Bucket (*Repert. Pharm.* and *Chemiker Zeitung*).—The author dissolves 200 grms. of the acids in three times their weight of water and adds ammonia in slight excess in order to effect the complete solution of any crystalline lead sulphate which may be present. After the lapse of twenty-four hours the liquid is decanted, the sediment collected upon a filter, washed, and dissolved upon the filter in nitric acid. From this solution the lead is separated as sulphate by sulphuric acid and alcohol in the well-known manner and weighed. Such lead must have been originally present in the metallic state. The solution of ammonium citrate or tartrate serves for the determination of lead compounds. It is acidified with hydrochloric acid, precipitated with sulphuretted hydrogen water, and the lead compounds are converted into lead sulphate as above directed.

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[*] Whewell's "History of the Inductive Sciences," vol. ii., pp. 202—203.

[†] *Ibid.*, vol. ii., p. 201.

[‡] *Ibid.*, vol. ii., pp. 198, 199

[*] "The Correspondence of Richard Bentley, D.D.," vol. i., p. 70.

[†] "Theoria Philosophiæ Naturalis reducta ad unicam legem virium in natura existentium auctore P. Rogerio Josepho Boscovich, Societatis Jesu," 1st edition, Vienna, 1758; 2nd edition, amended and extended by the author, Venice, 1763.

## OBITUARY.

### THE LATE PROFESSOR TYNDALL.

On the evening of Monday, December 4th, British Science lost one of its most conspicuous representatives in the person of Dr. John Tyndall. The deceased had been suffering for some years from insomnia, and an overdose of chloral hydrate administered accidentally hastened his end. Tyndall was born in 1820, at Leighlin Bridge, in county Carlow. He appears to have been connected with William Tyndale, the martyred translator of the Bible into English.

Young Tyndall received his education at an Irish National School, and early showed an unusual aptitude and predilection for mathematical studies. In his nineteenth year he joined a division of the Ordnance Survey then stationed in the district. In this capacity he earned the good will of his superior, Lieut. Geo. Wynne, R.E. On quitting the Ordnance Survey, in 1843, he was engaged in the surveys necessitated by the Railway Mania. Here he encountered severe physical obstacles, but his resolution triumphed over all, and his plans and sections could always be deposited in time. It is recorded that he rejected all opportunities for private emolument.

In 1847, he accepted the appointment of teacher of physics at New Harmony, a college founded at Queenswood, Hants, by the socialistic apostle, Robert Owen. Here he became intimate with Dr. E. Frankland, who was in charge of the chemical laboratory. After the collapse of New Harmony, Tyndall and Frankland went to continue their studies at Marburg, under Bunsen. At the same time he was reading mathematics zealously, and making himself acquainted with the writings of Fichte and Goethe. These literary studies drew him in after life into a friendship with Carlyle.

His study of the phenomena of diamagnetism, undertaken at the suggestion of Knoblauch, brought him under the notice of Faraday. In 1851 he became acquainted with Ehrenberg, with whom he had frequent conversations on microscopic organisms. Among his other friends were Magnus, Du Bois Reymond, Clausius, Humboldt, and Helmholtz.

In 1853 he was elected Professor of Natural Philosophy at the Royal Institution. In 1855 he became Examiner under the Council for Military Education. Here he advocated a more liberal recognition of Science in the studies of Artillery officers and Engineers. On this subject he expressed himself with such freedom as to risk dismissal, which, however, did not take place.

In 1857 and 1858 Tyndall continued his studies on glaciation, which became his holiday subject.

In 1859 he took up the question of the absorption of radiant heat by gases and vapours, upon which he threw a new and a satisfactory light. For these researches he received, in 1864, the Rumford Medal of the Royal Society.

In 1863 he wrote his celebrated work "Heat considered as a Mode of Motion." In 1867 appeared the companion volume on "Sound," and in 1869—74 he published his lectures on Light. In these volumes he showed a wonderful skill in expounding physical phenomena and laws without a scaffolding of the higher mathematics.

In 1868 he took up the question of abiogenesis, and of the part played by microbia in the dissemination of epidemics. These results he expounded in his famous lecture on "Dust and Disease," delivered at the Royal Institution on January 21, 1870. His conclusions were supported on thousands of experiments, and though at first ridiculed by many medical and other scientific men, they are now universally accepted. It must be understood that Tyndall did not pose as the pioneer of the microbial theory of disease. But he did not blindly accept the teachings of Pasteur, Schrœder, and others. He appears here as—save the case of Helmholtz—the only mathematician who has done good service in any branch of biology.

Passing over Tyndall's valuable respirator, and his course of lectures in America, we must notice his Presidency of the British Association, at the Belfast Meeting (1874), and his celebrated Address. This oration excited the ire, firstly of the orthodox, and then—like the writings of Darwin—of the heterodox.

In 1876 Tyndall married Lady Louise Charlotte, eldest daughter of Lord and Lady Claude Hamilton.

A noteworthy phenomenon in Tyndall's life was his friendship for Carlyle. Of "the sage of Chelsea" he formed a more favourable estimate than is usually done. He defends Carlyle against the charge of being, like Socrates, an enemy of Science. His defence, however, can scarcely avail against certain well-known passages in Carlyle's own writings.

We cannot, in conclusion, proclaim Tyndall as an epoch maker in Science, but we must pronounce him the author of an abundance of most valuable research. He has at the same time made Science both more acceptable to, and more accepted by, the great bulk of the nation, by the masses as well as the classes.

We perceive that the German press speaks in terms of warm praise of John Tyndall, and of the services he has rendered to Science.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 21, November 20, 1893.

**A New Model of a Reverberatory Electric Furnace with Movable Electrodes.**—Henri Moissan.—The construction of this furnace requires the accompanying illustration. The furnace has a horizontal tube of coke. If this tube is inclined by 30° the furnace is converted at once into a continuous apparatus for the production of the refractory metals, into which the mixture of oxides to be reduced is allowed to slide, whilst the liquid metal flows off easily on this inclined plane. In this continuous electric furnace the thermic phenomena of the arc are completely separated from the electrolytic phenomena. With a current of 600 ampères and 60 volts it is easy to obtain in an hour a regulus of fused metallic chrome of about 2 kilos. The metal is received in a crucible of chromium sesquioxide, where it remains liquid long enough to become refined. It is then perfectly liquid, and after solidification it yields a white, very hard metal of a fine grain and taking a brilliant polish. The author indicates as a specimen of the experiments which he has in progress the preparation of carbon and vanadium silicides. If we place silicon in a boat of carbon in the midst of the tube heated with a current of 1000 ampères and 60 volts, we obtain on the upper surface prismatic needles of carbon silicide which reach the length of several m.m.

**Action Exerted by some Metals in the Acid Solutions of their Chlorides.**—A. Ditte and R. Metzner.—This paper will be inserted at considerable extent.

*Revue Universelle des Mines et de la Metallurgie.* Series 3, Vol. xxiv., No. 1.

**New Process for the Rapid Determination of Sulphur in Commercial Irons.**—H. A. Hooper.—From the Chemical News.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 92.

This issue contains no chemical matter.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxii., Part 4.

**Detection of Higher Alcohols in Ethyl Alcohol.**—Bardy (*Amer. Apotheker Zeitung*).—The author mixes the spirit in question with four and a half volumes of a saturated solution of sodium chloride and half a volume of water, and shakes out repeatedly with carbon disulphide. The latter, when separated from the brine, is mixed with some concentrated sulphuric acid. This is again separated from the carbon disulphide. The latter is entirely removed by forcing air into it. There is now added to the sulphuric acid an equal volume of glacial acetic acid, and the whole is boiled for fifteen minutes in a reflux condenser. If a quantity of saturated brine equal to the original volume of spirit is now added, the acetic ethers of the butylic and amylic alcohols present separate out in the state of oily drops. If we measure the volume in a narrow graduated tube and multiply by 0·8, we find the quantity of the higher alcohols originally present.

**Detection of Acetone.** — A. Schwicker (*Chemiker Zeitung*).—The author proposes its conversion into iodoform by iodine in presence of ammonia. Under these conditions no iodoform is obtained from ethylic alcohol.

**Determination of Sulphur in Organic Substances.**—Walter Hempel (*Zeit. Angew. Chemie*).—The author utilises Berthelot's proposal to effect the combustion in an atmosphere of oxygen. He finds that the process may be effected at the ordinary pressure, so that the use of the calorimetric bomb may be dispensed with.

**The Gunning-Kjeldahl Method of Determining Nitrogen.**—A. L. Winton, jun.—From the CHEMICAL NEWS.

**Determination of Malic Acid.**—C. Micko (*Zeit. d. Allgem. Oestern. Apotheker Vereins*).—Will be inserted in full.

**Determination of Succinic Acid.** — Alfred Rau (*Archiv. f. Hygiene*).—This memoir will be inserted in full.

**Studies on the Determination of Glycerin.**—E. Suhr (*Archiv. f. Hygiene*).

**An Improved Process for the Rapid and Certain Detection of Cholera Bacilli.** — R. Koch (*Zeit. f. Hygiene*).—Already inserted.

**Examination of Mace.**—Th. Waage (*Pharm. Centralhalle*).—For this paper we must refer to the original.

**Examination of Essential Oils.**—A series of extracts from a trade circular issued by Schimmel and Co., April, 1893.

**Execution of the Iodine Addition Method.**—P. Welmans (*Pharm. Zeitung*).—The author proposes as a solvent for mercuric chloride and iodine a mixture of equal volumes of pure acetic acid and acetic ether or ethylic ether. The solution is adjusted with sodium thiosulphate, the value of which has been ascertained by means of a standard solution of potassium dichromate. The temperature has a decisive influence on the determination of the iodine number. In every experiment the initial and final temperature must agree with that of standardising. A temperature of between 17° and 20° is most suitable. All operations must be effected only in bottles or flasks with ground glass stoppers.

**Examination of Lanoline.**—Liebreich and Berend (*Pharm. Zeitung*) contest the opinion of Mente that the anhydrous lanoline of Jaffé and Darmstädter contains ethyl alcohol.

**Analysis of Irons.**—A very extensive series of extracts rom *Stahl and Eisen*, the CHEMICAL NEWS, *Bull. de la Soc. de l'Ind. Minérale, Chem. Centralblatt, Trans. of American Institute of Mining Engineers, Journal of Chemical Society*; *Berg und Hüttenm.-Zeitung, Journal of Society of Chemical Industry, Comptes Rendus*, &c., forming a total too bulky for abstraction.

**The Centrifugal in the Service of the Examination of Urine.**—MM. Blix and Jolles.—Both authors admit that by means of a centrifugal apparatus small quantities of urinary deposits can be caused to subside rapidly, and thus rendered fit for microscopical and chemical examination. However, Jolles shows that the method is not suitable for quantitative determinations (*Vienna Med. Presse*).

**Determination of Acetone in Urine.**—R. Supino (*Revista Generale Italiana*).—The author adds to the distillate of the urine soda-lye and then solution of potassium iodide until the colour becomes blue, and then again alkali until the liquid is decolourised. The iodoform produced is shaken out with ether, the ether expelled by evaporation, the residue dissolved in strong alcohol and boiled with concentrated soda-lye (free from chlorine) for twenty minutes in a reflux refrigerator in order to convert the iodine into sodium iodide. After expelling the alcohol and acidifying the quantity of iodine, it is determined volumetrically with solution of silver. 1 c.c. of decinormal solution of silver indicates 1·93 m.grm. acetone.

**Detection of Biliary Pigment in Urine.**—O. Rosenbach (*Deutsche Mid. Wochenschrift*) tests for bile pigment by the cautious addition of a few drops of a 5 per cent solution of chromic acid. The urine turns green. Excess is to be avoided, as otherwise the colour is a brownish red. H. Rosin gives another test in the *Berlin Klin. Wochenschrift.*

**Detection of Hæmatoporphyrine in Urine.** — A. Garrod.—From the *Journal of Physiology.*

**Uroroseine.** — Dr. Rosin (*Deutsch. Med. Wochenschrift*).—This substance may be obtained from normal urine, but in large proportion from pathological specimens. Its properties have been accurately described by Nencki and Sieber in *Zeit. Anal. Chemie*, xxii., 300.

**Detection of Albumen in Urine.**—B. Vas (*Ungar. Archiv. f. Medicin*) finds the reaction with sulpho-salicylic acid especially trustworthy. He adds a 20 per cent solution of sulpho-salicylic acid to eight drops, when 0·003 per cent may be recognised. The disturbing influence of urinary mucus may be avoided by precipitation with magnesium sulphate and testing for serum albumen in the filtrate (" Hygeiea," April, 1892).

**Arsenical Poisoning.** — F. Strassmann (*Apotheker Zeitung*).—One of the pleas raised for the defence in case of the detection of arsenic in a corpse is that the arsenic may have been introduced after death (!). Strassmann shows that in cases of arsenical poisoning there is a uniform distribution of the poison in all the organs, whilst if arsenic is introduced after death it accumulates especially in the left kidney, the right kidney containing either mere traces or none at all.

**Career of Arsenious Acid in the Animal Organism.**—D. Vitali (*Bolletino Chemico-Farmaceutico*).—According to the author, arsenious acid in the organism is chiefly oxidised to arsenic acid and is then eliminated by way of the urine. Arsenic acid in the organism forms complicated compounds, in which it plays a part analogous to that of phosphorus in lecithine.

**Toxicological Importance of Copper.**—K. B. Lehmann and others. — From the *Eilfte Versamm. Bayer. Chemiker.*

**Atomic Weight of Boron.**—W. Ramsay and Emily Aston (from the CHEMICAL NEWS), also J. L. Hoskyns Abrahall (*Journal of the Chemical Society*) and E. Rimbach (*Berichte*). — These researches give the weight sought for respectively as :—10 966 (Ramsay and Aston), 10·825 (Abrahall), and 10·945 (Rimbach).

Determination of Mon-acid and Di-acid Phosphate in Urine.—E. Freund (*Centralblatt fur Medic. Wissenschaften*) first titrates total phosphoric acid with solution of uranium, precipitates the mon-acid phosphates with barium chloride, and titrates afresh the filtrate. The difference referred to equal quantities of urine show the proportion of mon-acid phosphate.

Detection of Carbamic Acid in Urine.—J. J. Abel and E. Drechsel (*Archiv. f. Physiologie*) stir up the recent urine with much thick freshly-prepared milk of lime, shake well for from five to ten minutes, and filter. The filtrate (which must not give a precipitate with lime-water) is shaken up for fifteen minutes with calcium chloride and some crystallised calcium carbonate in a stoppered vessel. After a brief subsidence in an ice-closet, the liquid is filtered into three times its volume of alcohol cooled down to 0°; after subsidence for several hours the flocculent precipitate is filtered by means of a Sprengel pump, washed with alcohol and ether, and dried in a vacuum. The precipitate contains any carbaminic acid as a salt of calcium.

Conditions of Solubility of Uric Acid.—G. Rüdel (*Archiv. Exp. Pathologie*).—The presence of urea renders uric acid incapable of precipitation, except in presence of excess of acid.

## MISCELLANEOUS.

The Municipal Chemical Office of the City of Breslau.—The *Chemiker Zeitung* announces that during the last year the following poisons have been detected in human bodies sent in for examination:—Arsenic, in three cases; alcohol, chloroform, and hydrocyanic acid each in one case; and carbon monoxide in three cases.

The Association of German Naturalists and Physicians.—According to the *Chemiker Zeitung*, the sixty-sixth meeting of this body will be held next year in Vienna, beginning on September 24. It will be remembered that "Naturalist" (Naturforscher) in the German language includes the followers of any of the natural and physical sciences.

The Antiseptic Action of Cresol. — Lacroix-Hunkiabeyendian (*Journal de Pharmacie et de Chimie*).—A mixture of ortho-, meta-, and para-cresol is found to exert a stronger action upon microbia (*Staphylococcus pyogenes aureus*, *Tetragenus prodigiosus*, and the bacilli of cholera and typhus) than any of the pure compounds used singly. The solubility of the cresols in water is increased by the presence of a small quantity of cresol-sodium.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Professor Dewar, Six Lectures (adapted to a Juvenile Auditory) on "Air—Gaseous and Liquid"; Professor Charles Stewart, Nine Lectures on "Locomotion and Fixation in Plants and Animals"; The Rev. Canon Ainger, Three Lectures on "The Life and Genius of Swift"; Mr. W. Martin Conway, Three Lectures on "The Past and Future of Mountain Exploration"; Professor Max Müller, Three Lectures on the "Vedânta Philosophy"; Professor W. H. Cummings, Three Lectures on "English Schools of Musical Composition" (with Musical Illustrations); The Right Hon. Lord Rayleigh, Six Lectures on "Light" (with special reference to the Optical Discoveries of Newton). The Friday Evening Meetings will begin on January 19th, when a Discourse will be given by Professor Dewar, on "Scientific Uses of Liquid Nitrogen and Air"; succeeding Discourses will probably be given by Mr. A. P. Graves, Mr. T. J. Cobden-Sanderson, Professor W. F. R. Weldon, Professor Silvanus P. Thompson, Professor John G. McKendrick, Dr. W. H. White, The Right Hon. Lord Rayleigh, and other gentlemen.

## MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 8. (Cantor Lectures). "The Art of Book and Newspaper Illustration," by Henry Blackburn.
—— Medical, 8.30
Tuesday, 12th.—Institute of Civil Engineers. 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
Wednesday, 13th.—Society of Arts, 8. "Carriage-way Pavements for Large Cities," by Lewis H. Isaacs.
—— Pharmaceutical, 8.
Thursday, 14th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
Friday, 15th.—Quekett Club, 8.

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## PROCESSES FOR MANUFACTURING GAS FROM OIL,

### WITH SPECIAL REFERENCE TO

## THE PEEBLES PROCESS.*

By W. IVISON MACADAM, F.R.S.E., F.I.C., F.C.S., &c.

That a rich illuminating gas could be obtained by the destructive distillation of oils has been known for many years. In the earlier experiments the ordinary greasy or fatty oils were employed, but the cost of material was so great that the works erected were rapidly closed. The oils used were principally colza or rape oil and train or whale oil. The amount of gas obtained was from 70 to 90 cubic feet per gallon of oil; whilst the illuminating power ranged from 30 to 70 candles. The cost was rarely below twenty-five to thirty shillings per thousand cubic feet. These fatty or greasy oils are combinations of the triatomic alcohol, glycerin ($C_3H_5(HO)_3$), with fatty acids, principally palmatic ($C_{16}H_{31},HO$), stearic ($C_{18}H_{35},HO$), and oleic ($C_{18}H_{33},HO$). When destructively distilled the glycerin passes, to a large extent, into the aldehyd acrolein ($C_3H_3O,H$); whilst the fatty acids yield a series of compounds of which the olefines form the greater part. The gas is therefore very rich in carbon, and burns with a smoky flame, requiring special burners for its consumption.

Next in time comes "coal oil." This substance is a very complex mixture of carbon and hydrogen compounds. It contains members of the benzol, paraffin, olefine, acetylene, and other series. It is obtained during the purification of ordinary coal-tar, and is sometimes used as an illuminating oil. The specific gravity runs from 840 to 850 (water 1000). It contains proportions of the lower members of the benzol, olefine, and paraffin series, which give it a low flashing-point (65° to 70° F.), and low burning point (70° to 80° F.). The yield of gas is, however, high, averaging over 100 cubic feet per gallon of oil, with an illuminating value equal to about 70 standard candles. The gas is rich in members of the olefine series, of which it contains over 45 per cent. It also contains some members of the paraffin series, but only small quantities of the acetylenes. By the newer processes this substance should give valuable results.

The most important classes of carbon and hydrogen compounds from which gas may be distilled are the petroleums and paraffins. The first of these terms is more strictly applied to certain naturally formed hydrocarbons found widely distributed over the surface of the globe. The term paraffin has been adopted for the materials derived from shales, &c., when these are destructively distilled in closed retorts with or without the admission of steam, and with or without the presence of air.

The natural hydrocarbons, whilst widely distributed, not only geographically but geologically, are found in large quantities only in a few localities. In Russia, the Baku deposits have been long known; in Burmah the substance has been worked for centuries; in Japan and China; in Egypt, &c. With the exception of the Russian deposits, all other localities fall into insignificance beside the enormous underground reservoirs discovered in America. The vastness of these American deposits of natural oil may, perhaps, be better understood when I state the area already proved, by boring and other means, is over 200,000 square miles, and that the production in the year 1882 reached a total of 30,460,000 barrels, or over 1,279,320,000 gallons, of which Pennsylvania alone sent out 1,174,757,220 gallons. Since then the output has decreased somewhat. In the case of Russia the export is gradually increasing. In 1882 the total number of gallons manufactured was only 200,000,000; in 1884 the amount had risen to 429,400,000 gallons.

The American petroleums consist, chemically, principally of true paraffins ($C_nH_{n_2+2}$), with an admixture of the olefines ($C_nH_{n2}$), and traces of the benzols ($C_nH_{n_2-6}$). The Russian naphthas, on the other hand, are, to a large extent, made up of olefines, with some benzenes, paraffins, and acetylenes. They contain little or no solid paraffin.

In America especially the lighter and more volatile members of the paraffin series (methane and ethane) are found in great quantities as natural gas, and are in admixture with hydrogen and small proportions of carbonic anhydride ($CO_2$). This natural gas is of high heating value, and is of the greatest importance in those works requiring a heat of great intensity, such as in the manufacture of steel.

Paraffin oils are obtained by the destructive distillation of shales in closed retorts. The total volatile matter in these shales varies greatly, but may be stated at from 16 to 28 per cent, with a probable average of 23 per cent. When heated in the retorts the yield of crude oil is about 12 to 13 per cent. The specific gravity is from about 860 to 880 (water 1000). The total production of crude oil, in Scotland, is equal to 60,000,000 to 62,000,000 gallons per annum. There is also produced during the shale distillation 4 to 6 per cent permanent gas. One sample of this gas gave, on analysis, the following results:—

| | |
|---|---|
| Carbonic anhydride .. .. .. | 15·40 |
| Hydrogen .. .. .. .. .. | 34·53 |
| Carbonic oxide .. .. .. .. | 10·72 |
| Methane .. .. .. .. .. | 4·02 |
| Nitrogen .. .. .. .. .. | 35·33 |
| | 100·00 |

The gas burns with a pale almost non-luminous flame, and is employed for heating the retorts, &c. It gives a hot flame, and is well suited for firing purposes. It is also used for lighting the crude retort benches, but for this purpose requires to be carburetted by passage through light naphthas. When the science of oil distilling was less perfectly understood, this gas was purified by means similar to those employed for coal-gas, and used for domestic lighting. Now the illuminating agents are almost perfectly separated, and the flame has become practically non-luminous.

Crude paraffin oil is made up chemically to a large extent of members of the olefine series, with less proportions of the paraffins and traces of benzols and some acetylenes. It differs, therefore, from the natural petroleum, which is more largely composed of true paraffins. The names, in fact, would be more descriptive if the term paraffin were confined to the American natural oil.

The American petroleum is not so readily broken up into a permanent gas. In some experiments I made with a sample of burning oil of 799 specific gravity I obtained 86 cubic feet of a 66½-candle gas per gallon of oil. The decomposition, moreover, was not so complete as with other oils, and consequently when stored the gas lost a greater proportion of its luminosity by condensation.

Crude shale oil may be distilled into permanent gas with good results, but as the material is either solid or semi-solid, it is very difficult to work, as even when heated it is liable to "set" in the small pipes leading to the retorts. In some tests made with an oil of 850 gravity, we obtained from the gallon 98½ cubic feet of permanent gas of 50 candle power. The crude oil contains impurities, from which it may be separated by distillation in a current of steam; and the resulting oil gives much better results when made into gas. During the oil

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* Report of Lecture delivered before the North of Ireland Association of Gas Managers, August, 1893.

distillation the gravity is reduced to close on 800, and the gallon of oil will then yield over 100 cubic feet of a 70-candle gas.

Such oils, however, are not well suited for gas making, with the older forms of apparatus, as, containing the light volatile hydrocarbons, they are highly inflammable, and are dangerous to store. At the same time they contain the valuable "burning" oils, the solid paraffins, and heavy lubricating oils. These bodies are generally extracted from the shale oil before the residue is employed for gas making. The process varies in different works, but generally consists first in a distillation with steam, then in a treatment with sulphuric acid, and afterwards with soda to remove certain nitrogenous-alkaloidal bodies belonging to the pyridine series, &c., and tar acids of the carbolic and other series. The oil is then again distilled, but the distillate is "cut" into two portions; (*a*) a light oil, containing naphtha, burning oil, and intermediate oils, with some of the softer solid paraffins; and (*b*) a heavy oil, from which is extracted intermediate and lubricating oils, and solid paraffins of the higher fusing-points. These various fractions are extracted after repeated treatments with sulphuric acid and soda, followed by distillation, this latter aided by a current of steam. The products then are:—

1. Light oils or naphthas (750 gravity).
2. Burning oils (805 to 830 gravity).
3. Intermediate oils (840 to 870 gravity).
4. Lubricating oils (870 to 890 gravity).
5. Solid paraffin.

The light oils or naphthas may be distilled into permanent gas, but are more usefully employed as solvents for india-rubber, as turpentine substitute for paints, for carburetting (mechanically) water-gas, &c.

The burning oils give a good yield of illuminating gas. An oil of 815 gravity gave us 100 cubic feet per gallon of a gas of 63-candle power, and a second oil of 830 gravity yielded over 100 cubic feet of a 50-candle power gas for the gallon of oil.

The solid paraffins are too valuable to be economically distilled, even were the mechanical difficulty of their solid condition overcome.

The oil from which the solid paraffins of higher fusing-points have been extracted is "green" oil, and may be readily converted into gas. A sample of 884 oil gave 102 cubic feet of gas, having an illuminating value of 53-candle power. This oil, however, still contains some of the softer solid paraffins, which can be removed by freezing when the liquid becomes "blue" oil. This class of oil is also used for gas making, with good results. The average result obtained by us may be stated at 128 cubic feet of gas of 54-candle power per gallon of oil. After further purification and distillation this oil becomes "lubricating" oil of various gravities and "body." A lubricating oil of 873 gravity readily gave 102 cubic feet of a gas 61-candle power; whilst a heavy lubricating oil, of 894 gravity, gave 94 cubic feet of a 57-candle gas per gallon of oil distilled.

It is, however, with the intermediate oils that the present, as well as the future, of oil-gas making will remain. These oils, after the most careful fractionation and treatment, are too heavy to burn in ordinary lamps, as their viscosity is too high to admit of their ascending the wick by their own capillarity. They may, however, be burned to advantage in specially-constructed lamps. They are also too light in body for use as lubricants, and were, therefore, almost waste substances. Before the days of oil-gas these oils were submitted to the process of "cracking," and in America this is still carried out. The method simply depends upon the fact that the higher members of the olefine series, when subjected to a prolonged application of radiant heat at or near their distillation point, are converted partly into lower members of the same series, and partly into marsh-gas (methane). The paraffins present are almost entirely converted into lower members of the olefine series. By this means the gravity is lowered and the viscosity destroyed. After a treatment with acid and soda and a distillation, they may be used for burning in ordinary paraffin lamps. They, however, never give satisfaction, as, being so largely composed of olefines, they form combinations with the vitriol used in the treatment, and on being burned the wicks become loaded with sulphur compounds, and are charred. The products of combustion also contain much sulphurous anhydride ($SO_2$). Since the demand for gas-oil has increased, cracking, in this country at least, has entirely disappeared, and the intermediate oils have now a distinct value in themselves. The flashing-point of the intermediate oils runs from 230° F. to 250° F., and the firing-point over 280° F. There is, therefore, no danger from volatile inflammable vapours lodging in the store tanks. The yield of gas per gallon of oil is about 94 cubic feet, and the quality close on 60 candles. The gas consists of about 35 to 37 per cent of olefines—with methane, hydrogen, and some benzenes and acetylenes.

Until within the last few years oil known as "gas oil" was on the market. This product was obtained by distilling the mixed tars formed by the addition of the acid and soda during the various stages of refining the paraffin oils. The gas-oil was an amber-coloured liquid; contained leucolines and pyridines from the soda-tar and hydrocarbons especially rich in carbon. It burned with a very smoky, sooty flame, and gave a gas rich in acetylenes. The manufacturers now find that it is more economical to burn the tars as fuel below the boilers and stills. It is injected by a current of steam, and is a valuable fuel.

The gas made from oil is used either directly as an illuminant or to enrich other gas of a poorer quality. In the processes I propose to describe I have purposely left out those forms of apparatus which enrich poor illuminating gas by passing it directly through highly volatile hydrocarbons. Such processes are purely mechanical, and result simply in the suspension of the highly volatile liquid in a large body of a permanent gas. The Patentees of oil-gas apparatus have invariably attempted to distil the oil by one operation into gas, and their processes require a considerable heat on the retorts. As by-products they obtain a condensable tar of benzolnaphthalene character and more or less carbon (*not coke*). The Peebles process, as I propose to show, makes no such claim, and the only by-product is a hard and valuable coke.

Of the first class I will describe the processes of (*a*) Pintsch, (*b*) Keith, (*c*) Alexander and Paterson (Kirkintilloch), (*d*) Brooks, and latterly I will take up the Peebles process and show how it differs from the other methods.

Pintsch's apparatus is especially constructed to work burning and lubricating oils, or oils of the class intermediate between burning and lubricating. It is not adapted for crude oils or other oils which set to solid or semi-solid masses at ordinary temperatures. The retorts are ⌓-shaped, and are worked in pairs. The higher retort has a tray placed in it, on which is received the oil to be distilled. The intention of the tray is to keep the cold oil from falling on the hot retort surface and probably damaging it. Besides this, however, it acts as a vapouriser and as a collector of much of the carbon deposited from the oil, and thus aids in cleaning the retort. The oil, having become vapourised and partially broken up or decomposed in this upper retort, passes by a neck-piece, situated at the back of the higher retort, downwards to the lower retort, where, meeting with a higher temperature, the decomposition into permanent gas is fully accomplished. The gas then passes to the tar pit, where some dark liquid is deposited, and thence to condensers where it is cooled, and to a washer and purifier, from which it goes to the gas-holder. The condensers have nothing very novel about them, but the washer deserves description. It consists of a cylindrical column, in which is suspended an iron tray with a corrugated under surface, so constructed as to spread the gas and compel it to come in contact with the water. The gas passes by perforations in the side of the tray to the upper gas chamber, and thence by a pipe to the purifier. This latter is of the usual pattern, except that the iron tray gives place to a basket-work square, on which is placed the mixture of oxide of iron and sawdust intended to remove any sulphur compounds that may be in the gas.

The quantity of gas produced by this apparatus may run as high as 90 cubic feet per gallon of oil, but in ordinary working from 80 to 85 cubic feet is looked upon as a fair return. For each 1000 cubic feet of gas made about 4 gallons of tar is obtained. This tar has not been very fully investigated, but in some experiments I made I was successful in isolating several members of the benzene series, some olefines and acetylenes, and a considerable proportion of naphthalene. It is said to find a market on the Continent, but, so far as my own experience goes, it is generally consumed as a fuel below the steam-boiler employed to compress the gas. It yields a good heat, and is well suited for the purpose. At the same time it appears to be a great pity that so much valuable material should be lost. Generally, the Pintsch gas is employed for the lighting of railway carriages, floating buoys, lighthouses, lightships, &c. In such cases the gas is compressed by powerful pumps into steel cylinders under a pressure of about 13 atmospheres. These store cylinders then supply the smaller portable cylinders, which, in the case of railway carriages, are generally fixed below the flooring. On the Thames and Clyde, as well as several other home rivers, Messrs. Pintsch have supplied floating buoys. These are generally spherical in form, with the lower part removed and an inverted saucer-shaped bottom rivetted on. This form of bottom is found the best to overcome the force of a current. The sphere is surmounted by an iron superstructure holding the lamp and lenses. In the newer form the gas receiver is an independent receptacle placed inside the outer sphere. By this means the risk of damage by collision is, to a great extent, overcome. These gas buoys are usually charged at a pressure of from 5 to 10 atmospheres; have a consumption of 0·75 cubic foot per hour; a flame with a candle power equal to about 5 standard candles, but which, by means of lenses, is increased to an apparent 17 to 20 candles; and burn night and day without recharging for fully 100 days. The buoys are recharged as nearly as possible each two months, but, having a much larger storage power, can be safely left for a much longer period. At first some difficulty was found in keeping the lights burning, but by a very simple form of concussion box this difficulty has been completely overcome, and I am informed by the inspector of the Clyde Navigation Trust that such a thing as a light becoming extinguished is unknown.

Besides these buoys, the Clyde Navigation Trust have several light towers, lighthouses, &c., working with the gas.

As showing the ease of working and saving of cost, I may instance the Garmoyle lightship, which previously required the regular attendance of a man and his wife, with an outlay for wages, oil, &c., of nearly £150 per annum. Now there is no attendant on board, and the gas is charged to two steel cylinders once each two months. The supply of gas is much in excess of the two months' requirements, and on one occasion the gas did not require replenishing till after fully three months, and then it was not exhausted. The cost for gas is about £12 to £16 per annum. The light burns continuously, and requires little or no attention.

All of the Clyde installations are fed from one gas-works, situated at Port Glasgow, the gas being carried to the various points by a specially-constructed screw steamer, the "Torch." This beautiful little vessel carries two steel cylinders, which are kept fully charged; and the boat is always ready to go to any point should an accident occur. So far only one instance has taken place in which her services have been necessary.

The Pintsch gas is also used for gas engines, at Toward Point and Little Cumbrae. The apparatus at Toward Point is of one horse-power and works a fog bell; the Little Cumbrae gas-engine is of six horse-power, and is used to blow the siren.

During the compression of the gas a certain amount of loss is sustained by the condensation of part of the luminants. This condensation is equal to about one gallon of hydrocarbon per 1000 cubic feet of gas, and the loss of illuminating power is nearly 20 per cent. The initial candle power of the gas is equal to about 50 standard candles for each 5 cubic feet burned.

The products under this system may shortly be said to be, for 12½ gallons of oil, 1000 cubic feet of gas, 4 gallons of tar, and 1 gallon of hydrocarbon. The hydrocarbon consists largely of benzenes.

Many statistics have been published by the various companies using this apparatus as to the cost of the gas. Two of the largest railway companies put the cost, after deducting residuals, but exclusive of distribution or interest on plant, at 6s. per thousand cubic feet, and their make at from 78 to 80 cubic feet per gallon of oil.

(To be continued).

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# THE ORGANIC ELEMENTS.

By W. PREYER.

THE fourteen organic elements of the first order take a prominent position in the genetic system. They all belong to the first and second generation, consequently to the oldest elements. Thirteen of them are placed on the first, the second, and the third stage of condensation, iron alone is found on the fourth, and their distribution among the seven branches is characteristic. To Branch I. belong Na and K; to II., Mg, Ca, and Fe; to IV., C and Si; to V., N and P; to VI., O and S; to VII., F and Cl; whilst H precedes all the others. Group III. contains no organic element of the first order. The differences between the atomic weights are:—

$$\left.\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right\}16{\cdot}08\qquad \begin{matrix}\left.\begin{matrix}\mathrm{Mg}\\ \mathrm{Ca}\end{matrix}\right\}15{\cdot}76\\ \left.\mathrm{Fe}\right\}15{\cdot}92\end{matrix}\qquad \left.\begin{matrix}\mathrm{C}\\ \\ \mathrm{Si}\end{matrix}\right\}16{\cdot}33.$$

$$\left.\begin{matrix}\mathrm{N}\\ \mathrm{P}\end{matrix}\right\}16{\cdot}98\qquad \left.\begin{matrix}\mathrm{O}\\ \mathrm{S}\end{matrix}\right\}16{\cdot}06\qquad \left.\begin{matrix}\mathrm{F}\\ \mathrm{Cd}\end{matrix}\right\}16{\cdot}4.$$

The elements of terrestrial protoplasm, as it now exists, display more manifold relations than to all the other elements, and agree with the assumption that the organic elements, before being so condensed as they are now on the earth's surface, formed protoplasms capable of persisting at higher temperatures, and being possibly biophores—vehicles of life in other places.

In order to obtain a nearer insight into the properties of the elements of protoplasm which enable it to form living bodies, I have for many years collected facts on the occurrence of the organic elements of the second order in the protoplasm of plants and animals. The following are the elements in question:—L, Bo, Al, Ti, Cr, Mn, Cu, Zn, As, Br, Rb, Sr, I, Cs, Ba, whilst the remainder seem to occur in living plants and animals only if their compounds have been artifically introduced.

The question in how far the organic elements of the second order may, at least, temporarily replace or substitute those of the first order has, in spite of its profound interest, been as little thoroughly examined as the other on which it depends, that the compounds of the majority of all the elements, those especially with higher atomic weights and low specific heats, are not capable of being assimilated by the animals and plants living at present upon the surface of the earth.

Too little has also been ascertained with certainty on the occurrence of the organic elements in the sun, and in other fixed stars, to allow us to conclude with certainty as to the composition of the protoplasms of remote worlds capable of living at high temperatures. But, as I have shown elsewhere, it can no longer be doubted that prior to the present telluric protoplasm and zoöplasm, there lived another ultimately derived from the sun.

In this respect it is noteworthy that of the fourteen elements of our organism eight have been certainly recognised in the sun (H, Na, K, Mg, Ca, Fe, Si), three do not seem present in the solar atmosphere (N, P, S), three (O, Cl, F) are doubtful.—*Das Genetische System der Chemischen Elemente.*

## DETERMINATION OF MALIC ACID.

By C. MICKO.

As the extractive substances and inorganic acids present in wine are partially precipitated on throwing down the malic acid with lead acetate, the author's method is so contrived that phosphoric and sulphuric acids, as also much of the organic substances, are partly thrown down and partly destroyed. This is especially the case with tannin and the colouring-matter of wine, so that at last the filtrates are either faintly coloured or, as in ciders, almost colourless. The extractive matters which remain in solution, if acidulated with acetic acid and treated with lead acetate and an excess of alcohol at from 80 to 85 per cent, give no precipitates.

The determination, in which it must be remembered that any chlorides present may occasion a separation of lead chloride, is arranged as follows:—

100 c.c. of wine are evaporated down to a few c.c. on the water-bath, the residue is put in a flask, and allowed to stand for an hour at the common temperature with the addition of 4 to 5 c.c. bi-normal sulphuric acid. It is then gradually mixed, with constant agitation, with 50 c.c. of strong alcohol and 50 c.c. of ether and allowed to stand for from six to ten hours. During this time, the constituents insoluble in ether-alcohol have been deposited. We filter, wash the precipitate with ether-alcohol, add 100 c.c. water to the filtrate in order to prevent the etherification of the acids, distil off the greater part of the ether-alcohol on the water-bath, and lastly expel the last traces of the alcohol by distillation in a vacuum. After refrigeration to from 50° to 60°, the chlorine is precipitated with a fresh preparation of silver sulphate, using the smallest possible excess. At this temperature, in presence of free sulphuric acid, there occurs only a slight reduction of the silver.

After the silver chloride is deposited, the filtrate is neutralised with potassium carbonate, and evaporated down to a small volume. The solution is then further treated exactly as directed in *Zeit. Anal. Chemie* (xxxi., 465) for separating malic acid from succinic, citric, and tartaric acid. In case of ciders, the portion taken for analysis should not exceed 50 c.c.—*Oester. Apotheker Vereine.*

## THE TOXICOLOGICAL SIGNIFICATION OF COPPER.

This much-contested question, with especial reference to preserved vegetables (peas, &c.),—which are obtained of a fine green colour by an addition of copper salts—has been closely examined by Prof. K. B. Lehmann (*Elfte Versammlung der freien Verieinigung Bayerscher Vertreter der Angewandten Chemie*, p. 16) and others. It is known that Galippa found in grain, per kilo., from 5 to 10 m.grms.; flour, 8 m.grms.; bread, from 1 to 4 m.grms.; potatoes, 2 m.grms.; green beans, 2·2 m.grms.; lentils, 6·8 m.grms.; beans, from Soissons, 11 m.grms.; cocoa, 11 to 29 m.grms.; chocolate, 5·20 m.grms. copper. In 1 kilo. of beef there is found 1 m.grm. copper; in 1 kilo. of human liver, from 3 to 15 m.grms. Sheeps' liver, according to Lehmann's analysis, contains, per kilo., 18 m.grms.; calf liver, 48 m.grms.; ox liver, 51 m.grms.; dogs, and cats' liver, 10 to 12 m.grms.; ox, sheep, and rabbit kidney, 3·8 to 8 m.grms. of copper. On the regular consumption of small quantities of copper, the proportion of copper in the urine is not increased, as it seems to be retained by the liver. The results in the last experiments remained the same, whether the Bunsen burners used in the necessary chemical operations were of brass—a material containing copper—or of iron.

In a kilo. of fruit coloured, according to the rules of art, with copper salts, Mayrhofer found only 151—76 m.grms.; in vegetables, from 25 to 45 m.grms. copper. He is of opinion that 25 m.grms. of copper is perfectly sufficient for the purpose of the green staining, the fixation of the chlorophyll, according to Tschirch, as copper phyllocyanate. The proportion of copper in vegetables carelessly stained with copper may reach 270 m.grms. per kilo. without being especially recognised by the taste.

According to Lehmann's own experiments, which agree with numerous other scientific observations, small doses of copper, even on prolonged ingestion, are endured without any inconvenience. Doses of copper salts which introduce into the system, along with the food, about 100 m.grms. of copper, occasion light disturbances of health, a bad after-taste, vomiting, &c., but nothing further.

Small doses of copper have proved so harmless that Mayrhofer's notion—"On the basis of present experience, a proportion of 25 m.grms. copper in 1 kilo. of preserved vegetables cannot be regarded as injurious to health,"—was unanimously adopted at the Congress of Bavarian Chemists.

## FOGS, CLOUDS, AND LIGHTNING.*

By SHELFORD BIDWELL, M.A., LL.B., F.R.S.

The air, as every one knows, is composed almost entirely of the two gases, oxygen and nitrogen. It also contains small quantities of other substances, of which the chief are carbonic acid gas and water vapour, and it is the latter of these constituents, water vapour, or "steam," as it is sometimes called, that will principally concern us this evening.

The quantity of invisible water vapour which the air can at any time take up depends upon the temperature; the higher the temperature of the air the more water it can contain. The proportion, however, never exceeds a few grains' weight of water to a cubic foot of air. Air at any temperature, containing as much water as it can possibly hold, is said to be "saturated," while the temperature at which air containing a certain proportion of water becomes saturated is called the "dew point."

The water vapour contained in the atmosphere plays a very important part in many natural phenomena. Among other things, it is the origin of clouds and of fogs. If a body of air containing water in the form of invisible vapour is quickly cooled to a temperature below its dew point, a portion of the vapour becomes condensed into a number of minute liquid particles of water, forming a visible mist, which, when it is suspended in the upper regions of the air, is called a cloud, and when it rests upon the surface of the earth is only too familiarly known as a fog.

The cooling of water-laden air may be brought about in various ways, resulting in the formation of clouds of several distinct characters. [Photographic examples of cumulus, stratus, and cirrus clouds were exhibited upon the screen.] For experimental purposes a small body of

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* A Lecture delivered at the Royal Institution of Great Britain, May 5, 1893.

air may be most conveniently cooled by allowing it to expand. I have here a flask of air which can be connected with the partially exhausted receiver of an air-pump. Inside the flask is an electrical thermometer or thermo-junction, the indications of which can be rendered evident to all present by the movement of a spot of light upon a scale attached to the wall. A deflection of the spot of light to the left indicates cold, to the right heat. When the stop-cock is opened, so that a portion of the air escapes from the flask into the air-pump receiver, you see at once a violent movement of the spot of light to the left, showing that the expansion of the air is accompanied by a fall of temperature. If more air from the room is allowed to enter the flask, the spot moves in the opposite direction.

The large glass globe, upon which the beam from the electric lantern is now directed, contains ordinary air kept in a state of saturation, or nearly so, by the presence of a little water. You will observe that although heavily laden with water vapour the air is perfectly transparent. If, now, we turn a tap and so connect the globe with the exhausted receiver, the air expands and becomes colder; the space inside the globe is no longer able to hold the same quantity of water as before in the form of vapour, and the excess is precipitated as very finely-divided liquid water,—water dust it may be called,—which fills the globe and is perfectly visible as a cloud or mist. In a few minutes the cloud disappears, partly, no doubt, because some of the particles of water have fallen to the bottom of the vessel, but chiefly because the air becomes in time warmed up to its original temperature (that of the room), and the suspended water is converted back again into invisible vapour.

Now let us repeat the experiment, and before the cloud has time to disperse let us admit some fresh air from outside. The cloud, as you see, vanishes in an instant. The compression of the air raises the temperature above the dew point, and the small floating particles of water are transformed into invisible vapour.

I once more rarefy the air, and admit a fresh supply while holding the flame of a spirit lamp near the orifice of the inlet pipe, so that some of the burnt air is carried into the interior of the globe. When the air is again expanded a cloud is formed, which is, as you observe, far more dense than the others were. It appears on examination that the increased density of this cloud is not due to the condensation of a greater quantity of water. Little, if any, more water is precipitated than before. But the water particles are now much more numerous, their increased number being compensated for by diminished size. Within certain limits the greater the number of particles into which a given quantity of water is condensed the greater will be the apparent thickness of the mist produced. A few large drops will not impede and scatter light to the same extent as a great number of small ones, though the actual quantity of condensed water may be the same in each case.

Then comes the question, why should the burnt air from the flame so greatly increase the number of the condensed drops? An answer, though perhaps not quite a complete one, is furnished by some remarkable experiments made by M. Coulier, a French professor, nearly twenty years ago. He believed his experiments pointed to the conclusion that water vapour would not condense at all, even at temperatures far below the dew point, unless there were present in the air a number of material particles to serve as nuclei, around which the condensation could take place. All air, he says, contains dust; by which term he does not mean such dust as is rendered evident in this room by the light scattered along the track of the beam issuing from the electric lantern, which consists of comparatively gross lumps of matter, but particles of ultra-microscopical dimensions, "more tenuous than the motes seen in a sunbeam." It is upon such minute specks of matter that water vapour is condensed. Anything that increased the number of dust particles in the air increased the density of the condensation by affording a greater number of nuclei. Air in which a flame had been burnt he supposed to be very highly charged with finely-divided matter, the products of combustion, and thus rendered extraordinarily "active" in bringing about condensation. And that, according to Coulier's view, is the reason why such a dense fog was formed when air which had been contaminated by the spirit flame was admitted to our globe.

On the other hand, air, even burnt air, which has been filtered through tightly-packed cotton-wool, is found to be perfectly inactive. No cloud or mist will form in it, however highly it may be super-saturated. Coulier explained this fact by supposing that the process of filtration completely removed all dust particles from the air.

On the table before you is a globe containing air which has been thus treated, and which is kept saturated by a little water. When this globe is connected with the exhausted receiver, no trace of any mist is produced: the air remains perfectly clear. We will now admit a little of the ordinary air from outside, and again cool it by expansion. Quite a respectable cloud is thereupon formed in the globe.

The experiments of Coulier were repeated and confirmed by Mascart. The latter also made one additional observation, which may very probably turn out to be of great importance. He found that ozone, or rather strongly ozonised air, was a very active mist producer, and that, unlike ordinary air, it was not deprived of its activity by filtration.

Four or five years later, all the facts which had been noticed by Coulier, and others of an allied nature, were independently discovered by Mr. Aitken, who has devoted much time and study to them and made them the foundation of an entirely new branch of meteorology.

Later, perhaps, we may see reason to doubt whether all the conclusions of Coulier and Aitken are quite accurate, especially as regards the action of so-called products of combustion.

What has been said so far applies equally to the generation of clouds and of country fog, for a pure unadulterated fog, such as occurs in rural districts, consists simply of a cloud resting upon the surface of the earth. The fogs, however, which afflict many large towns, and London in a marked degree, appear to possess a character peculiar to themselves. They are distinguished by a well-known colour, which has sometimes been likened to that of pease soup: their density is abnormal, so is their persistence; and they often occur when the temperature of the air is considerably above the dew point. But what renders them especially objectionable is their acrid and corrosive quality, in virtue of which they exert a highly deleterious action upon animal and vegetable life.

The uncleanness of a town fog is of course due to the sooty and tarry matters with which it is charged, and which are derived from the smoke of innumerable fires. Its other and more mischievous specialities are mainly attributable to certain products of the combustion of sulphur, a substance which exists in relatively large proportions (from half to one per cent) in nearly all varieties of coal.

We may make a sample of London fog in the glass globe by burning a little sulphur near the orifice of the inlet pipe while air is being admitted; and in order to prevent the entrance of any solid particles of sublimed sulphur, we will filter the air through a little cotton-wool. The fog formed when the air is expanded far exceeds in density any we have yet seen. The globe appears almost as if it were filled with something that could be cut with a knife.

This is hardly the time or the place to discuss the possible methods by which town fogs might be abolished as such, or rendered as innocuous as those of the country. It is impossible to doubt that year by year they are increasing in virulence, and when the burden of the evil becomes too grievous to be borne, as is likely to be the case before many more winters are passed, the remedy will perhaps be found in the compulsory substitution of gas for coal as the ordinary domestic fuel.

Everyone has noticed how dense and dark a thunder-cloud is. It shuts out daylight almost as if it were a solid substance, and the glimmer that penetrates it is often imbued with a lurid or copper-coloured tint.

I had always found it rather difficult to believe that these peculiarities were due simply to the unusual extent and thickness of the clouds, as is commonly supposed to be the case, and it occurred to me about three years ago that perhaps some clue to the explanation might be afforded by the electrification of a jet of steam. On making the experiment I found that the density and opacity of the jet were greatly increased when an electrical discharge was directed upon it, while its shadow, if cast upon a white screen by a sufficiently strong light, was of a decidedly reddish brown tint.

As a possible explanation of the effect, I suggested that there might occur some action among the little particles of water of a similar nature to that observed by Lord Rayleigh in his experiments upon water jets. Perhaps you will allow me to show his fundamental experiment before further discussing the steam jet.

A jet of water two or three feet long is made to issue in a nearly vertical direction from a small nozzle. At a certain distance above the nozzle the continuous stream is found to break up into separate drops, which collide with one another, and again rebounding become scattered over a considerable space. But when the jet is exposed to the influence of an electrified substance, such as a rubbed stick of sealing-wax, the drops no longer rebound after collision, but coalesce, and the entire stream of water, both ascending and descending, becomes nearly continuous. Look at the shadow of the jet upon the screen, and notice what a magical effect the electrified sealing-wax produces.

There is one other point to which I wish to direct your particular attention. If the sealing-wax, or better, the knob of a charged Leyden jar, is held very close to the jet, so that the electrical influence is stronger, the separate drops do not coalesce as before, but become scattered even more widely than when no electrical influence was operating. They become similarly electrified and, in accordance with the well-known law, repel one another.

We will now remove the water jet, and in its place put a little apparatus for producing a jet of steam. It consists of a half-pint tin bottle, through the cork of which passes a glass tube terminating in a nozzle. When the water in the bottle is made to boil a jet of steam issues from the nozzle, and if we observe the shadow of the steam jet upon the screen we shall see that it is of feeble intensity and of a neutral tint, unaccompanied by any trace of decided colour. A bundle of needles connected by a wire with the electrical machine is placed near the base of the jet, and when the machine is worked electricity is discharged into the steam. A very striking effect instantly follows. The cloud of condensed steam is rendered dense and dark, its shadow at the same time assuming the suggestive yellowish brown colour.

I at first believed that we had here a repetition, upon a smaller scale, of the phenomenon which occurs in the water jet. The little particles of condensed water must frequently come into collision with one another, and it seemed natural to suppose that, like Lord Rayleigh's larger particles, they rebounded under ordinary circumstances, and coalesced when under the influence of electricity. The great majority of the small particles ordinarily formed consisted, I thought, of perhaps only a few molecules, which were dispersed in the air and again converted into vapour without ever having become visible, while the larger particles formed by their coalescence under electrical action were of such dimensions as to impede the more refrangible waves of light. Hence the brownish yellow colour.

Other explanations have been proposed. There is the molecular shock theory of the late R. Helmholtz (who, as it turned out, had studied electrified steam jets before I made my own experiments); I shall refer to his speculation later. And there is the dust-nucleus theory, which no doubt appears a very obvious one.

Though I knew that my own hypothesis was not quite free from objection, neither of these alternative ones commended itself to me as preferable; and so the matter rested until a few months ago, when the steam jet phenomenon was discussed anew in a paper communicated to the Royal Society by Mr. Aitken. Mr. Aitken said that he did not agree with my conjecture as to the nature of the effect. This led me to investigate the matter again, and to make some further experiments, the results of which have convinced me that I was clearly in error. At the same time it seems to me that the explanation which Mr. Aitkin puts forward is little less controvertible than my own. Mr. Aitken's explanation of the phenomenon is, like mine, based upon Lord Rayleigh's work in connection with water jets, but, unlike mine, it depends upon the experiment which shows that water particles when strongly electrified are scattered even more widely than when unelectrified. He believes, in short, that electrification produces the effect, not by promoting coalescence of small water particles, but by preventing such coalescence as would naturally occur in the absence of electrical influence. In the electrified jet, he says, the particles are smaller but at the same time more numerous; thus its apparent density is increased.

The chief flaw in my hypothesis lies in the fact that the mere presence of an electrified body like a rubbed stick of sealing wax, which is quite sufficient to cause coalescence of the drops in the water jet, has no action whatever upon the condensation of the steam jet. There must be an actual *discharge* of electricity. But it is by no means essential, as Mr. Aitken assumes, that this discharge should be of such a nature as to electrify, positively or negatively, the particles of water in the jet. If, instead of using a single electrode, we employ two, one positive and the other negative, and let them spark into each other across the jet, dense condensation at once occurs. [Experiment.] So it does if the two discharging points are removed quite outside the jet. [Experiment.] A small induction coil giving sparks an eighth of an inch in length causes dense condensation when the electrodes are more than an inch distant from the nozzle and on the same level. [Experiment.] In one experiment a brass tube two feet long was fixed in an inclined position with its upper end near the steam jet, and its lower end above the electrodes of the induction coil. In about three seconds after the spark was started dense condensation ensued, and it ceased about three seconds after the sparking was stopped. No test was needed, though in point of fact one was made, to show that the steam was not electrified to a potential of a single volt by this operation. And the time required for the influence to take effect showed that whatever this influence might be it was not induction.

The inference clearly is that in some way or other the action is brought about by the air in which an electrical discharge has taken place, and not directly by the electricity itself. The idea has no doubt already occurred to many of you that it is a dust effect. Minute particles of matter may be torn off the electrodes by the discharge, and form nuclei upon which the steam may condense. The experiments of Liveing and Dewar have indeed shown that small particles are certainly thrown off by electrical discharge, and the idea that such particles promote condensation appears to be supported by the fact that if a piece of burning material, such as touch-paper, is held near the jet so that the products of combustion can pass into it, thick condensation is produced. [Experiment.]

From a recent paper by Prof. Barus, published in the *American Meteorological Journal* for March, it appears that he also is of opinion that such condensation is in all cases due to the action of minute dust particles. Yet it is remarkable that Mr. Aitken, the high priest and chief apostle of the philosophy of dust, gives no countenance to the nucleus theory. He does not even advert to its possibility. I imagine that his experiments have led him, as mine have led me, to the conclusion that it is untenable. And this not only in the case of electrical discharge, but also in the case of burning matter.

If we cause an electrical discharge to take place for some minutes inside a suitably arranged glass bottle, and then, ten or fifteen seconds after the discharge has ceased, blow the air from the bottle into the steam jet, the condensation is not in any way effected. Yet the dust could not have subsided in that time. And again, if we fill another large bottle with dense clouds of smoke by holding a bundle of burning touch-paper inside it, and almost immediately after the touch-paper is withdrawn, force out the smoke-laden air through a nozzle, upon the jet—you can all see the black shadow of the smoke upon the screen—nothing whatever happens to the jet. Yet a mere scrap of the paper which is actually burning, though the ignited portion may not be larger than a pin's head, at once darkens the jet. Dead smoke (if I may use the term) exerts little or no influence by itself: there must be incandescent matter behind it. The question naturally arises, whether incandescent matter may not be sufficient of itself, without any smoke at all? We can test this by making a piece of platinum wire red hot and then holding it near the jet. It is seen to be quite as effective as the burning touch-paper. Yet here there can be no nuclei formed of products of combustion, for there is no combustion; there is simply ignition or incandescence.

One other point I may mention. It is stated by Barus in the paper above referred to that the fumes given off by a piece of phosphorus constitute a most efficient cause of dense condensation. This is true if they come directly from a piece of phosphorus; but if phosphorus fumes are collected in a bottle and then directed upon the jet, all traces of unoxidised phosphorus being first carefully removed, they are found to be absolutely inoperative. Phosphorus in air can hardly be said to be incandescent, though it is luminous in the dark; but it appears to act in the same manner as if its temperature were high.

All these facts seem to indicate that the several causes mentioned—electrical, chemical, and thermal—confer upon the air in which they act some temporary property—certainly not due to mere inert dust—in virtue of which it acquires an abnormal power of promoting aqueous condensation.

I thought that possibly some clue as to the nature of this property might be obtained by observing how some other gases and vapours behaved; but though the experiments I made perhaps tend to narrow the dimensions of the mystery, I cannot say that they have completely solved it. Indeed some of the results only introduce additional perplexities.

One of the most natural things to try is hydrochloric acid, which is known to have a strong affinity for water. If we heat a little of the acid solution in a test-tube, closed with a cork, through which a glass tube is passed, and direct the issuing stream of gas upon the jet, the densest condensation results. [Experiment.] The vapours of sulphuric and nitric acids also cause dense condensation, and I suppose both of these have an affinity for water. But so also, and in an equally powerful degree, does the vapour of acetic acid; yet the affinity of this acid for water, as indicated by the heat evolved when the two are mixed, is very small.

(To be continued).

**Variations of the Electric Conditions of High Regions of the Atmosphere.**—Ch. André.—The observations made showed that in fine weather the electric field does not necessarily increase with the altitude; it is the same at the same instant along the same vertical line.—*Comptes Rendus*, cxvii., No. 22.

## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 272).

C. *In Silver Bromide.*—If we expose silver bromide to the luminous rays it soon takes a blue greyish violet colour. This circumstance could not be overlooked in the investigation of its transparency. I have taken it so far into account as to reduce the exposure to a minimum in taking proofs. The very energetic sparks required were yielded by the above-named influence machine in connection with the Riess battery, but an inductorium was also employed. That my silver bromide screen must have assumed a colour is involved in the nature of the case, though the appearance was invariably contrary. Whether and in how far this colouration has been manifested in the absorption spectra it did not appear with certainty. But from one circumstance it may be inferred that it cannot have any great importance: the first and the last proof of the same screen did not essentially differ from each other.

The silver bromide for the screens, like that of the dry gelatin plate, was prepared with an excess of alkaline bromide, then washed, and the quartz plate used for the gelatin experiments coated therewith in a wedge-shaped layer and dried. As with the gelatin the coating of the plate was here also scraped away for a short extent, but only in three plates of increasing thickness. In this manner there were obtained three screens of different thickness for the rays. The thickness of these screens I have not been able to ascertain. The micrometer used for gelatin was quite useless on account of the liability of the coating of the plate to suffer injury, and the microscope was not certain enough. The use of the screen-plate in taking photographs was here as with gelatin. The proofs this time extended, not as in the former cases merely to the most refrangible ultra-violet, but they comprise the entire region from the Frauenhofer line D to the most refrangible rays of the aluminium.

I selected a wider spectral region than in the former proofs in order to acquire a better insight into the absorption relations of the silver bromide. The plates for this purpose contained erythrosine silver, which is well known to confer on bromine silver gelatin a remarkable sensitiveness to the yellow. For electrodes of the influence machine there were used two brass balls, which yielded a very efficient light. With a slit of 0·020 m.m. in width a single spark showed the spectrum in an almost uninterrupted succession of its lines from D to the wave-length 200 $\mu\mu$. For the most refrangible rays there were again used aluminium electrodes and the inductorium.

The total result of these proofs may be briefly summed up by saying that the silver bromide employed absorbs energetically all the rays of the region in question, even the cyanic blue, the green, and the yellow. Even the thinnest of the three layers, although to the eye strongly translucent, almost totally kept back the light of a single spark. The thicker layers did the same even on a rather more prolonged exposure. If we compare the spectra photographed with the same time of exposure we find that the absorption in silver bromide extends almost uniformly over the entire spectrum, but that the most refrangible rays from about the wave-length 210 $\mu\mu$ are rather less affected. This part of the spectrum is everywhere relatively rather more powerful than the other spectrum. Hence if the degree of the absorption afforded a certain standard for sensitiveness, the sensitiveness of silver bromide must decrease somewhat towards the more refrangible side. But I cannot ascribe too high a value to this

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II April, 1893).

conclusion, since it is sufficiently known from the foregoing that the lines of this region are in general paler than the others. In consequence the contrast of intensity between parallel proofs varies within such narrow limits that its estimation is always involved in considerable uncertainty.

According to these proofs we may assume that silver bromide is sufficiently sensitive for photographing the unknown ultra-violet, and that the want of intensity from which my proofs suffered must be referred to the presence of gelatin.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### THE ROYAL SOCIETY.

*Anniversary Meeting, November 30th, 1893.*

*Address of the President,* Lord Kelvin, D.C.L., LL.D.

(Concluded from p. 279).

Faraday, with his curved lines of electric force, and his dielectric efficiency of air and of liquid and solid insulators, resuscitated the idea of a medium through which, and not only through which but *by* which, forces of attraction or repulsion, seemingly acting at a distance, are transmitted. The long struggle of the first half of the Eighteenth Century was not merely on the question of a medium to serve for gravific mechanism, but on the correctness of the Newtonian law of gravitation as a matter of fact however explained. The corresponding controversy in the Nineteenth Century was very short, and it soon became obvious that Faraday's idea of the transmission of electric force by a medium not only did not violate Coulomb's law of relation between force and distance, but that, if real, it must give a thorough explanation of that law.* Nevertheless, after Faraday's discovery† of the different specific inductive capacities of different insulators, twenty years passed before it was generally accepted in Continental Europe. But before his death, in 1867, he had succeeded in inspiring the rising generation of the scientific world with something approaching to faith that electric force is transmitted by a medium called ether, of which, as had been believed by the whole scientific world for forty years, light and radiant heat are transverse vibrations. Faraday himself did not rest with this theory for electricity alone. The very last time I saw him at work in the Royal Institution was in an underground cellar, which he had chosen for freedom from disturbance; and he was arranging experiments to test the time of propagation of magnetic force from an electro-magnet through a distance of many yards of air to a fine steel needle polished to reflect light; but no result came from those experiments. About the same time, or soon after, certainly not long before the end of his working time, he was engaged (I believe at the shot-tower near Waterloo Bridge on the Surrey side) in efforts to discover relations between gravity and magnetism, which also led to no result.

Absolutely nothing has hitherto been done for gravity either by experiment or observation towards deciding between Newton and Bernoulli, as to the question of its propagation through a medium, and up to the present time we have no light, even so much as to point a way for investigation, in that direction. But for electricity and magnetism, Faraday's anticipations and Clerk-Maxwell's splendidly developed theory have been established on the sure basis of experiment by Hertz's work, of which his own most interesting account is this year presented to the world in the German and English volumes to which I have referred. It is interesting to know, as Hertz explains in his introduction, and it is very important in respect to the experimental demonstration of magnetic waves to which he was led that he began his electric researches in a problem happily put before him thirteen years ago by Professor von Helmholtz, of which the object was to find by experiment some relation between electromagnetic forces and dielectric polarisation of insulators, without, in the first place, any idea of discovering a progressive propagation of those forces through space.

It was by sheer perseverance in philosophical experimenting that Hertz was led to discover a finite velocity of propagation of electromagnetic action, and then to pass on to electromagnetic waves in air and their reflection, and to be able to say, as he says in a short reviewing sentence at the end of his eighth paper: "Certainly it is a fascinating idea that the processes in air which we have been investigating, represent to us on a million-fold larger scale the same processes which go on in the neighbourhood of a Fresnel mirror, or between the glass plates used for exhibiting Newton's rings."

Professor Oliver Lodge has done well, in connection with Hertz's work, to call attention* to old experiments, and ideas taken from them, by Joseph Henry, which came more nearly to an experimental demonstration of electromagnetic waves than anything that had been done previously. Indeed Henry, after describing experiments showing powerful enough induction due to a single spark from the prime conductor of an electric machine to magnetise steel needles at a distance of 30 feet in a cellar beneath with two floors and ceilings intervening, says that he is "disposed to adopt the hypothesis of an electrical plenum," and concludes with a short reviewing sentence: "It may be further inferred that the diffusion of motion in this case is almost comparable with that of a spark from a flint and steel in the case of light."

Professor Oliver Lodge himself did admirable work in his investigations with reference to lightning-rods,† coming very near to experimental demonstrations of electromagnetic waves; and he drew important lessons regarding "electrical surgings" in an insulated bar of metal "induced by Maxwell's and Heaviside's electromagnetic waves," and many other corresponding phenomena manifested both in ingenious and excellent experiments devised by himself and in natural effects of lightning.

Of electrical surgings or waves in a short insulated wire, and of interference between ordinary and reflected waves, and positive electricity appearing where negative might have been expected, we hear first, it seems, in Herr von Bezold's "Researches on the Electric Discharge" (1870), which Hertz gives as the third paper of his collection, with interesting and ample recognition of its importance in relation to his own work.

In connection with the practical development of magnetic waves, you will, I am sure, be pleased if I call your attention to two papers by Professor G. F. Fitzgerald, which I heard myself at the meeting of the British Association at Southport, in 1883. One of them is entitled "On a Method of Producing Electromagnetic Disturbances of comparatively Short Wave-lengths." The paper itself is not long, and I shall read it to you in full, from the "Report of the British Association," 1883:—"This is by utilising the alternating currents produced when an accumulator is discharged through a small resistance. It is possible to produce waves of as little as 2 metres wave length, or even less." This was a brilliant and useful suggestion. Hertz, not knowing of it, used the method; and, making as little as possible of the "accumulator," got waves of as little as 10 c.m. wave-length in many of his fundamental experiments. The title alone of Fitzgerald's other paper, "On the Energy Lost by

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* "Electrostatics and Magnetism," Sir W. Thomson, Articles I. (1842) and II. (1845), particularly § 25 of Art. II.

† 1837, "Experimental Researches," 1161—1306.

* "Modern Views of Electricity," pp. 369—372.

† "Lightning Conductors and Lightning Guards," Oliver J. Lodge, D.Sc., F.R.S. Whittaker and Co.

Radiation from Alternating Currents," is in itself a valuable lesson in the electromagnetic theory of light, or the undulatory theory of magnetic disturbance. It is interesting to compare it with the title of Hertz's eleventh paper, "Electric Radiation"; but I cannot refer to this paper without expressing the admiration and delight with which I see the words "rectilinear propagation," "polarisation," "reflection," "refraction," appearing in it as sub-titles.

During the fifty-six years which have passed since Faraday first offended physical mathematicians with his curved lines of force, many workers and many thinkers have helped to build up the Nineteenth Century school of *plenum*; one ether for light, heat, electricity, magnetism; and the German and English volumes containing Hertz's electrical papers, given to the world in the last decade of the century, will be a permanent monument of the splendid consummation now realised.

But, splendid as this consummation is, we must not fold our hands and think or say there are no more worlds to conquer for electrical science. We do know something now of magnetic waves. We know that they exist in nature and that they are in perfect accord with Maxwell's beautiful theory. But this theory teaches us nothing of the actual motions of matter constituting a magnetic wave. Some definite motion of matter perpendicular to the lines of alternating magnetic force in the waves and to the direction of propagation of the action through space, there must be; and it seems almost satisfactory as a hypothesis to suppose that it is chiefly a motion of ether with a comparatively small but not inconsiderable loading by fringes of ponderable molecules carried with it. This makes Maxwell's "electric displacement" simply a to-and-fro motion of ether across the line of progagation; that is to say, precisely the vibrations in the undulatory theory of light according to Fresnel. But we have as yet absolutely no guidance towards any understanding or imagining of the relation between this simple and definite alternating motion, or any other motion or displacement of the ether, and the earliest known phenomena of electricity and magnetism—the electrification of matter, and the attractions and repulsions of electrified bodies; the permanent magnetism of loadstone and steel, and the attractions and repulsions due to it: and certainly we are quite as far from the clue to explaining, by ether or otherwise, the enormously greater forces of attraction and repulsion now so well known after the modern discovery of electromagnetism.

Fifty years ago it became strongly impressed on my mind that the difference of quality between vitreous and resinous electricity, conventionally called positive and negative, essentially ignored as it is in the mathematical theories of electricity and magnetism with which I was then much occupied (and in the whole science of magnetic waves as we have it now), must be studied if we are to learn anything of the nature of electricity and its place among the properties of matter. This distinction, essential and fundamental as it is in frictional electricity, electro-chemistry, thermo-electricity, pyro-electricity of of crystals, and piezo-electricity of crystals, had been long observed in the old-known beautiful appearances of electric glow and brushes and sparks from points and corners on the conductors of ordinary electric machines and in exhausted receivers of air-pumps with electricity passed through them. It was also known, probably as many as fifty years ago, in the vast difference of behaviour of the positive and negative electrodes of the electric arc lamp. Faraday gave great attention to it ("Experimental Researches," Series 12 and 13, Jan. and Feb., 1838) in experiments and observations regarding electric sparks, glows, and brushes, and particularly in his "dark discharge" and "dark space" in the neighbourhood of the negative electrode in partial vacuum. In [1523] of his 12th series he says, "The results connected with the different conditions of positive and negative discharge will have a far greater influence on the philosophy of electrical science than we at present imagine." His "dark discharge" ([1544—1554]) through space around or in front of the negative electrode was a first instalment of modern knowledge in that splendid field of experimental research which, fifteen years later, and up to the present time, has been so fruitfully cultivated by many of the ablest scientific experimenters of all countries.

The Royal Society's *Transactions* and *Proceedings* of the last forty years contain, in the communications of Gassiot (*Roy. Soc. Proc.*, x., 1860, 36, 269, 274, 432), Andrews and Tait (*Ibid.*, x., 1860, 274; *Phil. Trans.*, 1860, 118), Cromwell Varley (*Roy. Soc. Proc.*, xix, 1871, 236), De la Rue and Müller (*Ibid.*, xxiii., 1875, 356; xxvi., 1877, 519; xxvii., 1878, 374; xxix., 1879, 281; xxxv., 1883, 292; xxxvi., 1884, 151, 206; *Phil. Trans.*, 1878, 55, 155; 1880, 65; 1883, 477), Spottiswoode (*Roy. Soc. Proc.*, xxiii., 1875, 356, 455; xxv., 1875, 73, 547; xxvi., 1877, 90, 323; xxvii., 1878, 60; xxix, 1879, 21; xxx., 1880, 302; xxxii., 1881, 385, 388; xxxiii., 1882, 423; *Phil. Trans.*, 1878, 163, 210; 1879, 165; 1880, 561), Moulton (*Roy. Soc. Proc.*, xxix., 1879, 21; xxx., 1880, 302; xxxii., 1881, 385, 388; xxxiii., 1882, 453; *Phil. Trans.*, 1879, 165; 1880, 561), Plücker (*Roy. Soc. Proc.*, x., 1860, 256); Crookes (*Ibid.*, xxviii., 1879, 347, 477; *Phil. Trans.*, 1879, 641; 1880, 135; 1881, 387), Grove (*Roy. Soc. Proc.*, xxviii., 1878, 181), Robinson (*Ibid.*, xii., 1862, 202), Schuster (*Ibid.*, xxxvii., 1884, 78, 317; xlii., 1887, 371; xlvii., 1890, 300, 506), J. J. Thomson (*Ibid.*, xlii., 1887, 343; xlix., 1891, 84), and Fleming (*Ibid.*, xlvii., 1890, 118), almost a complete history of the new province of electrical science which has grown up, largely in virtue of the great modern improvements in practical methods for exhausting air from glass vessels, by which we now have "vacuum tubes" and bulbs containing less than 1-190,000th of the air which would be left in them by all that could be done in the way of exhausting (supposed to be down to 1 m.m. of mercury) by the best air-pump of fifty years ago. A large part of the fresh discoveries in this province have been made by the authors of these communications, and their references to the discoveries of other workers very nearly complete the history of all that has been done in the way of investigating the transmission of electricity through highly rarefied air and gases since the time of Faraday.

Varley's short paper of 1871, which, strange to say, has lain almost or quite unperceived in the *Proceedings* during the twenty-two years since its publication, contains an important first instalment of discovery in a new field—the molecular torrent from the "negative pole," the control of its course by a magnet, its pressure against either end of a pivoted vane of mica according as it is directed by a magnet to one end or the other, the shadow produced by its interception by a mica screen. Quite independently of Varley, and not knowing what he had done, Crookes was led to the same primary discovery, not by accident, and not merely by experimental skill and acuteness of observation. He was led to it by carefully designed investigation, starting with an examination of the cause of irregularities which had troubled* him in his weighing of thallium; and, going on to trials for improving Cavendish's gravitational measurement, in the course of which he discovered that the seeming attraction by heat is only found in air of greater than 1-1000 (Crookes, "On the Viscosity of Gases at High Exhaustions," § 655, *Phil. Trans.*, Feb., 1881, 403) of ordinary density; and that there is repulsion increasing to a maximum when the density is decreased from 1-1000 to 36-1,000,000, and thence diminishing towards zero as the rarefaction is farther extended to density 1-20,000,000. From this discovery Crookes came to his radiometer, first without and then with electrification, powerfully aided by Sir George Stokes (*Phil. Trans.*, clxxii., 1881, 387, 435); and he brought all his work more and more into touch with the

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* Tribulation, not undisturbed progress, gives life and soul, and leads to success when success can be reached, in the struggle for natural knowledge.

kinetic theory of gases; so much so that when he discovered the molecular torrent he immediately gave it its true explanation—molecules of residual air, or gas, or vapour projected at great velocities* by electric repulsion from the negative electrode. This explanation has been repeatedly and strenuously attacked by many other able investigators, but Crookes has defended it ("Address to the Institute of Telegraphic Engineers," 189 ), and thoroughly established it by what I believe is irrefragable evidence of experiment. Skilful investigation perseveringly continued brought out more and more of wonderful and valuable results:—the non-importance of the position of the positive electrode; the projection of the torrent *perpendicularly* from the surface of the negative electrode; its convergence to a focus and divergence thenceforward when the surface is slightly concave; the slight but perceptible repulsion between two parallel torrents due, according to Crookes, to negative electrifications of their constituent molecules; the change of direction of the molecular torrent by a neighbouring magnet; the tremendous heating effect of the torrent from a concave electrode when glass, metal, or any ponderable substance is placed in the focus; the phosphorescence produced on a plate coated with sensitive paint by a molecular torrent skirting along it; the brilliant colours—turquoise-blue, emerald, orange, ruby-red—with which grey colourless objects and clear colourless crystals glow on their struck faces when lying separately or piled up in a heap in the course of a molecular torrent; "electrical evaporation" of negatively electrified liquids and solids (*Roy. Soc. Proc.*, June 11, 1891); the seemingly red-hot glow, but with no heat conducted inwards from the surface, of cool solid silver kept negatively electrified in a vacuum of 1-1,000,000 of an atmosphere, and thereby caused to rapidly evaporate. This last-mentioned result is almost more surprising than the phosphorescent glow excited by molecular impacts in bodies not rendered perceptibly phosphorescent by light. Both phenomena will surely be found very telling in respect to the molecular constitution of matter and the origination of thermal radiation, whether visible as light or not. In the whole train of Crookes's investigations on the radiometer, the viscosity of gases at high exhaustions, and the electric phenomena of high vacuums, ether seems to have nothing to do except the humble function of showing to our eyes something of what the atoms and molecules are doing. The same confession of ignorance must be made with reference to the subject dealt with in the important researches of Schuster and J. J. Thomson on the passage of electricity through gases. Even in Thomson's beautiful experiments showing currents produced by circuital electromagnetic induction in complete poleless circuits, the presence of molecules of residual gas or vapour seems to be *the essential*. It seems certainly true that without the molecules there could be no current, and that without the molecules electricity has no meaning. But in obedience to logic I must withdraw one expression I have used. We must not imagine that "presence of molecules is *the* essential." It is certainly *an* essential. Ether also is certainly *an* essential, and certainly has more to do than merely to telegraph to our eyes to tell us of what the molecules and atoms are about. If a first step towards understanding the relations between ether and ponderable matter is to be made, it seems to me that the most hopeful foundation for it is knowledge derived from experiment on electricity in high vacuum; and if, as I believe is true, there is good reason for hoping to see this step made, we owe a debt of gratitude to the able and persevering workers of the last forty years who have given us the knowledge we have; and we may hope for more and more from some of themselves and from others encouraged by the fruitfulness of their labours to persevere in the work.

## NOTICES OF BOOKS.

*The Magic Lantern, its Construction and Use.* By A Fellow of the Chemical Society. London: Perkin, Son, and Rayment. Small 8vo., pp. 140. Second Edition.

The magic lantern has now become a most valuable aid to the lecturer and the teacher. It gives far clearer and more intelligible illustrations than can be produced by means of the chalk and black-board, or even by ready-made diagrams. The microscope and the spectroscope are, of course, still as necessary as ever, or rather more necessary; but for placing our results before an audience, or even a numerous class, we must have the lantern.

The work before us gives a very full and practical description of the instrument and its manipulation. With one passage we take the liberty of disagreeing. Says the author: "The earnest worker, in whatever branch he may be engaged, likes to be self-dependent as far as possible." But the earnest worker likes to economise time, and does not want to be detained from actual investigation by preparing his requisites. We should, on this principle, recommend the lanternist, whenever possible, to buy compressed oxygen in cylinders.

Where manganese peroxide is used for the production of oxygen care should be taken that it is not contaminated with native antimony sulphide, a powder very similar in appearance. This impurity, which is sometimes present not from fraudulent intention, but from carelessness, has occasioned serious explosions.

In fine, we must pronounce this little book a most useful guide for lecturers, or for men of science who have to read papers before a Society.

*Foundations of the Molecular Theory:* comprising Papers and Extracts by John Dalton, Joseph Louis Gay-Lussac, and Amadeo Avogradro (1808—1811). Edinburgh: W. F. Clay. London: Simpkin, Marshall, and Co. (Ltd.). 1893.

This little work is one of the "Alembic Club Reprints." It gives, in order of time, the papers which exhibit the development of the idea of a connection between the number of particles in different gases and their volume.

Dalton, it will be seen, doubts the accuracy of Gay-Lussac's results. Avogadro accepts at once Dalton's theory and Gay-Lussac's facts, and reconciles them by drawing a distinction between the atom and the molecule of an elementary gas. Ampère's letter to Berthollet (1814) has not been here inserted, as it leaves the question exactly as it had been already done by Avogadro, who had drawn identical conclusions from identical premises.

*Agricultural Journal published by the Department of Agriculture of the Cape Colony.* Vol. vi., No. 20.

This paper continues to show great energy. We find that the steel-coloured ladybird, *Orcus chalybeus*, a native of Australia, is now being successfully employed to make war upon the scale insects on the orange and lemon trees. It is to be hoped that this species has not the cannibal propensity of some of the English ladybirds, the larvæ of which greedily devour the pupæ.

The necessity of tree-planting in South Africa is ably insisted upon. The introduction of goats into the Colony was a capital error.

There are complaints of "wireworm" attacking and injuring sheep. The insect (?) in question surely cannot be the *Elater* larva which is so destructive to root-crops.

It is a curious and most unpleasant fact that, if sheep have been exposed to a period of insufficient food, there

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* Probably, I believe, not greater in any case than 2 or 3 kilometres per second.

occurs in their wool a weak spot which is almost fatal to its utility for manufacturing purposes.

It is not edifying to learn that, as far as fruits are concerned, colonial produce is placed on the same footing as that from alien countries!

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*Spirits and the Manufacture of Cognac.* ("Les Eaux-de-Vie et la Fabrication du Cognac"). With Thirty-nine Figures inserted in the Text. By A. Baudoin, Director of the Public Laboratory of Agricultural and Industrial Chemistry at Cognac. Paris: J. B. Baillière et Fils. 1893.

M. Baudoin, whose official position and wide experience give him an exceptional opportunity to do justice to his subject, has produced a most valuable work on ardent spirits, with especial attention to the brandies of Cognac.

He gives a general account of spirituous liquors, the production of which he traces back to the most remote antiquity. He distinguishes grain-spirits, the spirits obtained from stone-fruits, the rums and tafias, the spirits distilled from cider and those from wine. He is evidently aware of root-spirits,—les eaux-de-mort, as they might fairly be called,—distilled from potatoes and beet-root, but he does not honour them with a special chapter.

Concerning the celebrity of Cognac, the author gives an amusing anecdote. Mgr. Cousseau, a former bishop of Angoulême, used to tell that, dining one day at Rome with some cardinals, he was questioned as to the locality of his see. "I am bishop of Angoulême and the Charente," said he. But as no one seemed to understand he added "I am also bishop of Cognac." At this name all the guests exclaimed, Cognac! Cognac! Cognac! Oh, what a superb bishopric!

The distillation, the composition, and the adulterations of brandies are fully described. It is remarkable that the finest Cognacs are produced by small cultivators who use a very simple plant. But we hear a very similar statement concerning Irish whiskies. The product of the small stills, "potheen," is often found superior to that produced with the most elaborate and costly plant.

Several German recipes are here given for counterfeiting Cognac. But a totally spurious Cognac is even manufactured in the Vaterland, distilled—would it have been imagined?—from the wines of Gruenberg, in Silesia!

M. Baudoin, we suspect, scarcely sees the full absurdity of manufacturing a superior brandy from a wine which in Germany has been proverbial for its unparalleled vileness. There are several grades of Gruenberg, the worst of which is so harsh that if a glass of it is poured over a man's neck he dies of strangulation!

Our author, though not ignoring the evils of alcoholism, maintains that under certain conditions a small dose of "veritable Cognac" is a valuable medicine. Hence, according to the pundits of "Teetotalism," there can be for him and his book no salvation.

To analysts who are called upon to examine spirits and to spirit merchants M. Baudoin's work will prove of great value.

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# CORRESPONDENCE.

## EASY RULES FOR CONVERTING THERMOMETRICAL DEGREES.

*To the Editor of the Chemical News.*

Sir,—Regarding the rules for converting thermometrical degrees from Centigrade to Fahrenheit and from Fahrenheit to Centigrade in Mr. G. Watmough Webster's letter of Nov. 10th (Chem. News, lxviii., 234).

After carefully comparing them with other simple rules for the same purpose by doing examples for both high and low temperatures mentally, I can see very little in them to make them preferable. The following formulæ are very simple, and they, as well, need no "expert reckoner," and can be used "without even needing pencil and paper." I include formula for Reaumur scale.

$$\frac{F-32}{9} = \frac{C}{5} = \frac{R}{4}$$

These formulæ are easily remembered, since everyone knows 9 degrees of F. equal 5 of C. or 4 of R. The rule would be—

*F. to C.*—Add 32, divide by 9, and multiply by 5.
*C. to F.*—Divide by 5, multiply by 9, and add 32.
*R. to C.*—Divide by 4 and multiply by 5.
&c., &c.

However, I prefer to picture the formulæ I have given in my mind and work out mentally.—I am, &c.,

Milton L. Hersey.

Canadian Pacific Rly. Testing Laboratory,
Montreal, November 27, 1893.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 22, November 27, 1893.

The mayor of Angers invited the Academy to be represented at the inauguration of the statue of Chevreul, which took place on December 3.

Preparation of Metallic Lithium.—M. Gantz.—This paper will be inserted in full.

Improvement of Dietetic and Lubricating Oils by an Electric Treatment.—L. A. Levat.—Having placed a column of olive oil of rancid taste and dark colour at the negative electrode of a voltameter impelled by a small Siemens machine (magnetic type of feeble voltage), the author put the voltameter in tension until the column of water situate under the column of oil was completely electrolysed. The oil was much lighter in colour. It had become rather turbid, probably from a mechanical mixture of water. The flavour was completely modified, having become almost mild, with a slight remnant of a very agreeable piquancy. He submitted to hydrogenation a score of ill flavoured samples of various sources, and had constantly succeeded in purifying their taste and their colour. With care the oil does not become turbid, but remains limpid. In the second place he made a series of experiments on lubricating oils of bad quality, containing at least 5 per cent of free acid. The acidity always decreased in the minimum propoition of 1/5. On submitting the same oil to electrolysis a second time, the acidity was diminished by 3/10.

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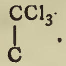
Anilide of Gallic Acid: its Ethers and its Salts.—P. Cazeneuve.—A substance, first obtained by Schiff, has received the industrial name of gallanol. The author shows that gallanol is identical with the anilide of gallic acid, and that gallic blue has a constitution analogous to that of gallocyanine. He describes a number of the compounds of this substance. With zinc acetate gallanilide forms the three compounds which are theoretically possible. Gallanilide also forms insoluble compounds with many alkaloids. Quinine and strychnine in an aqueous saline solution give with gallanilide precipitates comparable to the tannates.—*Bull. de la Soc. Chim. de Paris*, ix.—x., No. 22.

**Chloralose.**—M. Hanriot and Ch. Richet.—In a former paper the author has indicated the physiological properties of the two isomers resulting from the union of glucose and chloral, chloralose and parachloralose. Chloralose, $C_8H_{11}Cl_3O_6$ is slightly soluble in water and ether, soluble in alcohol, and melts at 187°. Parachloralose is insoluble in most solvents, and melts at 227°. Chloralose, parachloralose, and all their derivatives contain the three chlorine atoms of the chloral, and it is evident that the chloral unites with the glucose by its aldehyd group, and that chloralose must contain the group—



$$\begin{array}{c} CCl_3 \\ | \\ C \end{array}$$

**A Ptomaine Extracted from the Urine in Influenza.**—Dr. A. B. Griffiths and R. S. Ladell.—The ptomaine extracted from the urine in cases of influenza is a white substance crystallising in prismatic needles, soluble in water, and of a slightly alkaline reaction. It forms a hydrochlorate, a chloroplatinate, and a chloraurate, all crystalline. It gives a brownish precipitate with phosphotungstic acid, a yellowish with phosphomolybdic acid, a yellow with picric acid, and a red with tannic acid. The composition of this base is $C_9H_9NO_4$. It is poisonous, inducing a strong fever and death in eight hours. It is not met with in normal urine.

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*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. ix. and x., Nos. 20 and 21.

**Isoconicine.**—A. Ladenburg.—The author repeats here the theoretical views which, he considers, may explain the nature of isoconicine. He has endeavoured to split up hydroquinaleine, but has not succeeded in obtaining an active base.

**Acrylic Isomers of Borneol.**—Ph. Barbier.—The essential oils of licari, coriander, and roses consist almost exclusively of definite principles corresponding to the formula $C_{10}H_{18}O$. They are licareol, coriandrol, linalol, geraniol, and rhodinol. The author has examined licareol at great length.

**The Separation and the Volumetric Determination of Lead.**—MM. Zindemann and Motten.—This paper will be inserted in full.

## NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Brewing.**—Can any reader please inform me—(1) What is generally used in fining sour ale? (2) What is the composition generally used to give a froth to ale?—Hydrogen.

## MEETINGS FOR THE WEEK.

Tuesday, 19th.—Institute of Civil Engineers. 8.
—— Pathological. 8.30.
Wednesday, 20th.—Society of Arts, 8.
—— Geological, 8.
—— Microscopical, 8.
—— Meteorological, 8.
Thursday, 21st.—Chemical, 8. "The Oxidation Products of Corydaline," by Prof. Dobbie and A. Lauder.

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THE CHEMICAL NEWS.

Vol. LXVIII., No. 1778.

## ON THE ACTION OF REDUCING AGENTS ON NICKELO-POTASSIC CYANIDE.

By THOMAS MOORE.

In Crookes's "Select Methods" there is mentioned a test for nickel, proposed by Papasogli, which is performed by immersing a strip of zinc in a solution of nickelo-potassic cyanide containing ammonic chloride and free ammonia, whereby a red colouration is produced. Being somewhat curious as to the cause of this colour, I consulted several works on chemistry, amongst others the Dictionaries of Chemistry by Watts, Wurtz, and Dammar, but finding no mention of the reaction, decided to go into the matter. The results of some of the initial experiments, embodied in this communication, may not be without interest.

It was early noticed that the red colour was very fugitive, and that this evanescence was due to the absorption of oxygen from the air. The presence, too, of a large quantity of zinc compounds in solution tended to complicate many of the reactions, so that I was compelled to cast about for a more suitable reducing agent, and conduct the reduction in an atmosphere of hydrogen. The only substances which gave a rapid colouration were a solution of stannous chloride in sodic hydrate and sodium amalgam, although for obvious reasons the latter is preferable. By acting on moderately strong solutions of the nickelo-potassic cyanide by sodium amalgam added in successive portions, an intensely deep red solution is readily obtained, which gives precipitates on the application of different reagents totally different from those obtained with the ordinary $K_2NiCy_4$. The following are the most characteristic:—

Argentic nitrate, dissolved either in water, potassic cyanide, or ammonia, gives a heavy black precipitate of metallic silver.

Mercuric chloride, grey precipitate.

Plumbic acetate, black precipitate, insol. in KHO or $C_2H_4O_2$; decomposes on drying, leaving yellow PbO.

Bismuth nitrate, black precipitate.

Arsenic trioxide, deep brown precipitate.

Gold chloride slowly reduced.

Judging from these reactions, it is evident the body exercises a strong reducing action, as indeed it might have been supposed to do from the manner of its production, and from the avidity with which it absorbs oxygen and becomes decolourised by such substances as permanganate or bichromate of potash, peroxide of hydrogen, &c. The solution, when acidified, separates out an orange-yellow flocculent precipitate, which, when rapidly filtered off, and washed once or twice with cold water, dissolves in alkalis, forming a red solution. The precipitate darkens rapidly when exposed to the air, changing to a dirty blue colour, and decomposes completely on drying, even in a current of hydrogen, into what appears to be a mixture of oxide and cyanide of nickel.

To obtain an insight into its composition, a certain quantity of the well-reduced liquid was run into an ammoniacal solution of argentic nitrate, the precipitate filtered off and well washed, first with ammonia, and then with sodic hyposulphite, and then weighed. In the filtrate the nickel was then separated out and determined, and the ratio of the oxygen of the silver to the metallic nickel then calculated. By this means it was found that:—

| | |
|---|---|
| 58·7 grms. Ni required.. .. | 6860 c.c. oxygen. |
| 58·7 " " .. .. | 6405 " |
| 58·7 " " .. .. | 6670 " |
| 58·7 " " .. .. | 5988 " |

The oxygen absorption was then estimated in another way, by introducing a quantity of the solution into a burette filled with oxygen, and thoroughly agitating until the colour vanished, then balancing the pressures, and calculating the observed absorption to the dry gas at normal temperature and pressure. The colourless solution was then run into a receptacle, and the nickel estimated.

| Ni. | O found. C.c. | O calculated. C c. | O in 58·7 grms. Ni. C.c. |
|---|---|---|---|
| 0·08816 | 11·15 | 11·21 | 7425 |
| 0·0744 | 9·24 | 9·46 | 7290 |
| 0·0779 | 9·27 | 9·90 | 7539 |
| 0·0494 | 6·34 | 6·29 | 7533 |
| 0·0580 | 7·44 | 7·37 | 7353 |
| 0·0646 | 8·07 | 8·21 | 7333 |

It will be noticed that these numbers are very concordant considering the instability of the substance, but decidedly higher than those obtained by the silver method; this may perhaps be accounted for by the solvent action of the alkaline cyanide on the reduced silver; at the same time it is very evident that they agree very closely with two-thirds of a volume of oxygen to 58·7 parts (the atomic weight) of nickel; or, conversely, the red solution containing 3 atoms of nickel absorbs 2 atoms of oxygen in passing into the ordinary cyanide ($NiCy_2$), which would seem to indicate a compound ($Ni_3X_2$) where X is monatomic. Unfortunately, however, the excessive instability of the precipitate given by hydrochloric acid has up to the present excluded the possibility of an analysis, but I hope as the work proceeds to overcome this, and investigate the nature of some of the aforementioned precipitates, which latter, it may be mentioned, seem to be free from cyanogen.

Noumea, New Caledonia.

## ON THE OXIDATION OF COBALTO-CYANIDE OF POTASSIUM.

By THOMAS MOORE.

The formula given in text-books for the conversion of cobalto-cyanide of potassium into the corresponding cobalti-cyanide in presence of free hydrocyanic acid is usually expressed by two equations, the first representing the reaction without access of air,—

$$2K_4CoCy_6 + 2H_2O = K_6Co_2Cy_{12} + 2KHO + H_2;$$

the second exhibiting the oxidising influence of atmospheric oxygen, and consequent formation of water,—

$$2K_4CoCy_6 + 2H_2O + O = K_6Co_2Cy_{12} + 2KHO + H_2O.$$

From the latter it is given to understand that the $K_4CoCy_6$, in passing into $K_6Co_2Cy_{12}$, takes up one volume of oxygen; but actual experiments seem to demonstrate that whatever may be the composition of the resultant cobalti-cyanide, it is certainly accompanied by an absorption of oxygen greater than that required by the equation, which can only be regarded as true under certain conditions of temperature, &c.

In the course of some experiments on this subject it was noticed that on adding a mixture of sodic hydrate and potassic cyanide to a solution of cobalt, and well agitating until no further absorption took place, the liquid became of a deep brown-red colour, and an amount of oxygen was taken up much in excess of that required by the above formula, the quantity varying from 8000 to 9600 c.c. for 59 grms. of cobalt, whereas theory demands only 5600 c.c. On applying the same process with this difference, that the sodic hydrate was omitted, and the cobalt solution rather strongly acidified before mixing, a marked change was observed,—the solution became uniformly yellow and the absorption less, though still much in excess of the required quantity, as will be observed from the following figures taken at random from a considerable number of experiments :—

| | | | |
|---|---|---|---|
| Co employed .. .. | 0·0259 | 0·0614 | 0·0856 grms. |
| O absorbed at 0° and 760 m.m .. .. | 3·3 | 7·755 | 11·02 c.c. |
| O absorbed on 59 grms. Co. .. .. | 7503 | 7450 | 7516 c.c. |

Here it will be noticed that the consumption of oxygen is very regular, and would seem to indicate either the formation of some compound differing in composition from the usually accepted $K_6Co_2Cy_{12}$, or that some side reaction takes place. A number of experiments were performed to detect the latter, but saving the production of an insignificant amount of ammonia no other byproducts were found. It is probable, then, that at least two higher cobalti-cyanides exist; and this is supported by the fact that the above oxidised solutions, when boiled, evolve oxygen, and are then converted into the $K_6Co_2Cy_{12}$. Experiments are still being carried out to isolate these compounds in a pure state if possible, with the object of establishing their exact composition and properties.

Noumea, New Caledonia.

# PROCESSES FOR MANUFACTURING GAS FROM OIL,

## WITH SPECIAL REFERENCE TO THE PEEBLES PROCESS.*

By W. IVISON MACADAM, F.R.S.E., F.I.C., F.C.S., &c.

(Concluded from p. 285.)

**Keith's** apparatus differs in the form of retort from that previously described. It consists in a single through retort of ⌂-shape, but having in the centre, midway between the back and front, a depression. The oil is fed in at the front, and the gas passes out at the back of the retort. This class of apparatus has been adopted by the Northern Lights Commissioners for installations at Ailsa Craig and Langness, Isle of Man. In both cases the gas is used for gas-engines to blow sirens, and in the first case also for illumination.

I have no practical experience with this apparatus, but my father, Dr. Stevenson Macadam, under instructions from the Northern Lights Commissioners, went very fully into the merits of both Keith's and Pintsch's apparatus, and the following is a summary of his results :—

| *Keith's apparatus.* | No. 1. | No. 2. |
|---|---|---|
| Gas per gallon of oil.. | 85·05 cub. ft. | 84·82 cub. ft. |
| Illuminating value .. | 63·25 candles. | 59·52 candles. |
| *Pintsch's apparatus.* | | |
| Gas per gallon of oil.. | 90·70 cub. ft. | 103·36 cub. ft. |
| Illuminating value .. | 62·50 candles. | 59·15 candles. |

I am not aware of the quantity of tar produced in Keith's apparatus, nor am I aware how far the gas may be compressed, nor of the loss of illuminating value during compression. Before employing the gas for gas-engines, Mr. Keith dilutes it with one-half its volume of atmospheric air. The apparatus used is novel and efficient. The cost of the gas is stated to be 5s. 9d. per thousand cubic feet; but this sum does not include carriage of oil and coal, wear and tear of retorts, apparatus, &c., nor the cost of labour or distribution.

The Alexander and Paterson apparatus was intended at first for the production of gas from burning oil (815 specific gravity). Worked with this class of oil it readily gives 100 cubic feet of a 63-candle gas per gallon. Later, however, I recommended the use of intermediate oils, as gas can be produced from these at a much cheaper rate, owing to the smaller cost of material. In tests made with this apparatus, and intermediate oils of 864 gravity, 94 cubic feet of a 56-candle gas were easily obtained. The apparatus is simple, consisting of a retort, the door of which is perforated to allow of the introduction of tubes. The oil is passed by these tubes to the back of the retort, being largely vaporised *en route*; it then comes in contact with the heated sides of the retort, and is permanently broken up into a gas, which is drawn from the front of the retort. After condensation in upright pipes the gas is passed direct to the holder. Working with high-class intermediate oils well purified, the want of purifiers to remove sulphur compounds is not felt. The total amount of sulphur in the shale is not usually over 1½ per cent, and of this only 0·028 per cent can be traced to the crude oil: during the process of refining the most of this disappears. Where desired, however, the addition of a purifier is readily introduced. The apparatus is simple, easily worked, and especially suited for works or gentlemen's houses. It is working in several places, and is giving satisfaction. Where a pure oil-gas of high illuminating power is desired, and where such is not afterwards to be mixed with coal-gas, this apparatus is one of the best I know.

The Brooks's patent differs from all the foregoing, in so far as it is specially built for crude oils. The retort is most curiously shaped, in a zigzag fashion, and the special advantage of this form is said to lie in the greater contact of the oil with the heated sides of the retort. The process also differs from the others in so far as there is introduced a current of steam, which is broken up along with the oil, thus increasing the quantity of gas although lowering its lighting quality. The process is largely in use in America, and gives successful results. It is also patented in this country, but I am not aware of its being worked here. The peculiar form of retort is distinctly against its adoption, and I can see no reason for the form. Experience has clearly demonstrated that the process of gas-making from oil consists, chemically, in the degradation of higher carbon and hydrogen compounds to lower forms, accompanied by the production of bodies rich in carbon and free hydrogen, &c. These processes are best carried out by a heat radiated from a large surface, and not by direct contact with the metal. Direct contact leads to the production of much free hydrogen, and the deposition of free carbon in the retorts, with consequent loss of illuminating power. This has been fully brought out in experiments made by my father so long ago as 1872, with an apparatus packed with coke, and by myself in tests made with thin tubes. Further, the temperature required to break up oils into permanent gas of high illuminating value is an orange-red : whilst a white-heat increases greatly the gas produced, but practically destroys the illuminating power. With small tubes or zigzag apparatus it is almost impossible to regulate the temperature.

The Peebles process essentially differs from any of the other processes mentioned ; for, whilst these act by one direct heat action, the Peebles process, by means of a lower heat and constant return circulation of the condensable products, only gives a partial breaking up at each circulation. In the newer forms of apparatus, as at Galashiels, the coal-gas and oil-gas retorts are back to back, and the waste heat of the former serves to heat the latter. The retorts need not, however, be so placed, for at Peebles the coal-gas and oil-gas are made in the same oven, but for economical working the Galashiels setting should be best. The coal-gas retorts are of the usual ⌂-shape and size, and set in the ordinary way, whilst the best form of retort for the oil-gas is cylindrical. The Galashiels retorts are 9 feet long and 27 inches internal bore, and they are laid with a backward inclination. From the front of the retort there is an ordinary ascension, bridge, and dip-pipe to the hydraulic main. The condensers are nearly horizontal, with a slight upward

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* Report of Lecture delivered before the North of Ireland Association of Gas Managers, August, 1893.

tendency, and lead to a scrubber, on the principle adopted regularly in shale-oil works. The trays in the scrubber are fed with oil from a cistern attached to the upper part of the apparatus. From the scrubber the gas passes to the ordinary dry purifiers, where it meets with the coal-gas, and the mixed gases then go to the holder in the usual manner. The oil to the retort is obtained from what is called the compensating tank. In this tank the overflow from the hydraulic main, the liquids from the condensers, and the fresh oil are intermingled, with the result that a perfectly liquid substance is maintained throughout the whole working. Moreover, the apparatus, being of considerable size, acts as a settling tank, in which any solid carbonaceous matter is removed. The oil passes from the compensating tank by means of a pipe with regulating valve, to the ascension pipe, where the introduction of the liquid oil tends to wash the ascending gas, and remove any suspended carbonaceous particles. By this circulation method liquid residuals are avoided, and the residue left in the retort, when it is coked down, is a dense and very pure carbon with less than 0·5 per cent of ash, and readily burned. For this solid residue 20s. per ton has been regularly obtained at Peebles. It yields a smokeless flame of great heat intensity. The gas yield by this method runs, with "blue" oils, about 85 to 86 cubic feet per gallon, and the illuminating value when the gas is burned by itself is about 59-candle power. When burned in admixture with poorer illuminating gas the value is much greater. A month's actual working yielded—

| | | | | |
|---|---|---|---|---|
| Coal-gas .. | 1,217,600 | cubic feet of | 18 | candle power. |
| Oil-gas .. .. | 253,400 | ,, ,, | | |
| Total gases .. | 1,471,000 | ,, ,, | 30·51 | ,, |

| | Cubic feet. | Candles. |
|---|---|---|
| Coal-gas .. | $1{,}217{,}600 \div 5 = 243{,}530 \times 18$ | $= 4{,}383{,}360$ |
| Total gas .. | $1{,}471{,}000 \div 5 = 294{,}200 \times 30{\cdot}51$ | $= 8{,}976{,}043$ |

Therefore candle power from 253,400 cubic feet of oil-gas =4,592,682 candles, which, divided by the make (253,400 cubic feet) = 18·12 candles per cubic foot, and $\times 5 = 90{\cdot}60$ candle power as the true illuminating value of the oil-gas as an enricher. This gain in illuminating value by mixing is equal to 53·74 per cent. To explain this gain we need to consider several points. When any complex body is subjected to a sufficient amount of heat it is resolved into its elementary constituents, or into more simple bodies. If the heat applied be great enough, the ultimate particles will be driven so far apart that chemical union is rendered impossible. If, on the other hand, the heat is less, only partial decomposition results, and the substances produced are still compounds, although less complex than the original substances acted on. If the oil be subjected to the highly heated surface of a retort, the decomposition is almost complete—methane is formed, any oxygen goes into carbon monoxide or dioxide, hydrogen is set free, and all excess carbon is deposited as free carbon. If, on the other hand, the heat from the furnace is compelled to pass through the sides of the retort, and to be communicated to the atmosphere of the retort, which, in its turn, radiates the heat on the volatilised oil, the resulting decomposition will not be so complete, and the gases left will be more complex in nature, and more highly carbonaceous. To produce light from carbonaceous gases the carbon requires to be set free and then raised to a considerable temperature, so as to become incandescent. The incandescence may lead only to a glow, or, as the temperature rises, to a more decided light. If in the gas flame the heat, in this case derived from the burning of the hydrogen, carbonic monoxide, &c., is sufficient to produce a great enough temperature, the maximum of light will result. If these gases are too small in amount, then the flame becomes smoky and the light less. In oil-gas the last condition holds good, and the balance is brought about by the admixture with a poorly carbonaceous gas containing much hydrogen, and which on burning gives sufficient heat to render the excess carbon of the oil-gas incandescent. In other words, the excess of carbon in the oil-gas is rendered incandescent by the excess of heat-producing bodies in the poorer gas, and the result is an excess of light over that obtained from either gas alone. The 18-candle splint gas becomes valuable as an enricher on account of the excessive heat of its combustion, and the 59-candle power oil-gas enriches on account of its excessive carbon. Both gases are required to give the desired result, and both therefore have a claim on the excess of light obtained from admixture.

I have seen the Peebles process on several occasions, and can testify to the ease of working and regularity of product, and I feel sure that the process has a great future.

## DETECTION OF NITRONAPHTHALENE IN MINERAL OILS.

By NORMAN LEONARD, B.Sc.

Nitronaphthalene, the α-derivative, is frequently added to mineral oils for the purpose of removing the fluorescence, or "bloom." The following method for its detection depends upon the reduction of nitronaphthalene to naphthylamine.

A small quantity of the oil is gently warmed with zinc dust and dilute hydrochloric acid, and the mixture agitated from time to time. During this process the fæcal odour characteristic of α-naphthylamine will be perceived. After the reduction is complete, the acid aqueous liquid is drawn off by the aid of a separator. A portion of this liquid, when neutralised with ammonia, gives with ferric chloride a blue precipitate, which rapidly becomes purple. The remainder of the solution may be rendered alkaline with soda and extracted with ether. The latter is then evaporated and the residue dissolved in a little alcohol. On the addition of a drop of a solution of sodium nitrite, acidified with acetic acid, a yellow colour is produced which is changed to crimson by hydrochloric acid.

## ON ENDOTHERMIC REACTIONS EFFECTED BY MECHANICAL FORCE.*

### Part I.

By M. CAREY LEA.

In a preceding paper the effects of pressure on the silver haloids were described. These salts were readily blackened and so gave evidence of partial reduction. That investigation was undertaken with the object of bringing into complete harmony the effects upon these haloids of the different forms of energy. It had been previously shown with respect to all the other forms of energy that a slight impression made upon the haloids caused an effect not visible to the eye, but capable of indefinite increase by the application of a reducing agent. Also, it had been shown in the case of mechanical force that a slight application would cause an invisible effect which could be rendered evident by the application of a reducing agent. It seemed to follow almost necessarily that a powerful application of the same agent would bring about an effect visible to the eye. Experiment proved this to be the case.

It next appeared to be worth while to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. For the nature of these changes was something quite different from anything that had been previously described. In Prof. Spring's well-known investigation, combination was brought about between substances whose tendency to combine was restrained by

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* From the *American Journal of Science*, vol. xlvi., 1893.

their being in the solid form. This obstacle was removed by subjecting them to great pressure, and the same remark applies to some of the interesting experiments of Dr. Hallock. But the reduction of the silver haloids and other reactions presently to be described involve a quite different principle. The reactions produced are all endothermic; energy is consumed in accomplishing them, and this energy is supplied by mechanical force.

The combination of screw and lever affords the best means of applying pressure. A careful study as to the most suitable method of using these powers led to the selection of the vice form. It was found, however, that the manufacturers of heavy vices were unwilling to undertake to furnish vices with jaws that would sustain the force intended to be exerted on them, namely, that of a steel lever three feet long acting on a screw with six turns to the inch. I was therefore obliged to have them made under my own supervision. From a bar of tough rolled iron, 4 inches wide by 1½ thick, pieces about 18 inches long were cut and were forged into shape by a blacksmith; where the jaws met they were faced with steel, welded on. Suitable screws were easily obtained, but the nuts furnished with them having commonly only an inch in length would subject the thread to the danger of stripping. They were replaced with nuts 4 inches in length, thus distributing the strain over 24 turns of the thread. Two vices made in this way over a year ago have endured severe use without the least sign of strain.

With a lever having three feet in length between the centre of the screw head and the end at which the force is applied acting on a screw with six turns to the inch, the multiplication of force is 1357 times. As it is easy to apply a pull of a hundred pounds or even much more, a pressure of 135,000 pounds is easily obtained. As it was intended to keep the substances which were to be subjected to pressure from any contact that might affect them they were folded up in platinum foil and this was set in a V-shaped piece of soft sheet copper. The portion of material which received the pressure was about ½ inch long by ¼ wide; it consequently had an area of about ⅛ of a square inch. This limited surface received a pressure in the proportion of over a million pounds to the square inch or about seventy thousand atmospheres. These of course are calculated pressures subject to deduction for friction. The amount lost in this way cannot be determined, but is known to be considerable.

By the aid of these means the following results were obtained. In all cases the material was wrapped in either platinum or silver, usually platinum, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

*Silver sulphite* in platinum-foil was moderately darkened by two days pressure.

*Silver salicylate* was rendered very dark by two days pressure.

*Silver carbonate* was moderately darkened by a somewhat longer pressure.

*Silver tartrate* was not affected.

*Silver oxide* was thoroughly dried at 150°. A piece of platinum-foil was heated to redness and rapidly cooled, a portion of oxide was folded up in it and weighed. Weight found 0·7639. It was then subjected to very great pressure for four days. Weight found to be 0·7639, no change.

*Ferric oxide* recently precipitated and dried. No effect produced by pressure, no formation of ferrous oxide.

*Potassium Platinobromide.*—Where the pressure was greatest the brilliant red colour of this substance was blackened, not superficially only, but all through.

*Ammonium Platinochloride.*—Moderate but well-marked darkening.

*Potassium Chlorate.*—When this substance was subjected to pressure by itself no effect whatever was produced and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder and subjected to pressure, there was an evident formation of silver chloride. The material was no longer completely soluble in water, but left an abundance of white flakes which darkened when exposed to light.

*Mercuric oxide* requires a very high pressure to produce an effect upon it. It then darkens slightly, but very distinctly, and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it.

The darkened part as well as the rest dissolves without difficulty in acetic acid, and consisted therefore probably of traces of mercurous oxide and not metallic mercury.

*Mercurous chloride* showed no change.

*Mercuric Chloride.*—Corrosive sublimate, perfectly free from calomel, which commercial sublimate is very apt to contain, was subjected to great pressure and then treated with ammonia. As no darkening took place there had evidently been no reduction.

*Mercuric Iodide.*—Red mercuric iodide when subjected to very great pressure darkened considerably, and at points where the pressure was greatest it became absolutely black. It did not appear, however, that any iodine was set free, none could be extracted with alcohol.

*Mercuric Oxychloride* ($2HgO,HgCl_2$).—Heavy pressure caused much darkening.

*Sodium thiosulphate* with a moderate pressure compresses to a hard translucent cake, but does not undergo any decomposition.

To the foregoing cases are to be added those of the three silver haloids described in a previous paper; these blackened with a quite moderate pressure even in the case of the iodide.

Although in all these instances the darkening is well marked, still the actual proportion of material affected is small, so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done, and we are justified in concluding that many of the salts of easily reducible metals, especially of silver, mercury, and platinum, undergo reduction by pressure. Such reactions are endothermic, and *it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force precisely in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about.*

In the second part of this paper additional support will be adduced for these conclusions.

## THE DETERMINATION OF SUCCINIC ACID.

By ALFRED RAU.

The author studies the question in how far the quantity of succinic acid occurring during fermentation depends on the conditions in which the fermentation takes place. The methods hitherto employed seem to the author unsatisfactory. He finds that at 15° 100 parts of anhydrous ether dissolve 1·193 parts of succinic acid, whilst the same volume of alcohol at 96 vol. per cent dissolve 9·986, alcohol of 90 per cent 11·984, methylic alcohol 15·730, acetone, 5·544 parts. In benzol succinic acid is insoluble.

In a 2 per cent solution of neutralised succinic acid, lime water and calcium chloride did not produce a precipitate until after the addition of alcohol. Barium chloride, after alcohol, gave complete precipitation. Tartaric acid and malic acid are also completely thrown down in an alcoholic solution. Strontium chloride gives no precipitate, even in the presence of alcohol. Magnesium sulphate and magnesia mixture give no precipitate, and the latter precipitates tartaric acid but not malic acid. Zinc, cadmium, and aluminium sulphates occasion an imperfect precipitation, but not if malic and tartaric acid are present. Uranium acetate gives a precipitate, which is prevented by malic and tartaric acids. Stannous chloride and mercurous nitrate precipitate imperfectly (as also with tartaric and malic acid). Lead hydroxide and acetate precipitate imperfectly. Silver nitrate precipitates succinic acid perfectly, tartaric acid only in concentrated solutions, and malic acid only in such as are more concentrated than 1 : 800.

Nickel, manganese, glucinium, copper sulphate, and mercuric chloride produce no precipitate. Ferric chloride gives the well-known voluminous reddish-brown precipitate. Rau observed that the presence of sugar and glycerin did not interfere, whilst tartaric and malic acids hinder complete precipitation.

The author evaporates 100 c.c. of urine to a syrup, extracts repeatedly on the water-bath with boiling alcohol, and each time filters the alcoholic extract when cold. The extracts are mixed and distilled. The residue is dissolved in a little hot water; the solution, if it becomes turbid on cooling, is filtered, mixed with barium nitrate and 4 vols. of alcohol at 90 per cent, and well stirred. The precipitate, containing tartaric, malic, and succinic acid, after it has settled is filtered, washed with alcohol at 70 per cent, and heated for some time with a sufficient quantity of sodium carbonate.

The liquid is filtered, neutralised with nitric acid, evaporated down to a small volume, and, after neutralising with ammonia, treated with magnesia mixture. After subsiding for three to four hours the liquid is filtered from the precipitate which contains tartaric acid; the liquid is heated with potassa lye until all ammonia is expelled. The deposit is then filtered off, exactly neutralised with nitric acid, diluted to 100—150 c.c., and precipitated with solution of silver nitrate (1 : 20).

The precipitate is collected on a tared filter, washed, dried, and weighed. As a check it may be ignited in a porcelain crucible, and the metallic silver obtained is weighed. The results of the two weighings should correspond. If the liquid contains chlorine this element must be determined in 25 c.c., and the silver found as chloride must be deducted. — *Archiv. f. Hygiene* and *Zeitschr. f. Anal. Chem.*

## FOGS, CLOUDS, AND LIGHTNING.*

By SHELFORD BIDWELL, M.A., LL.B., F.R.S.

(Concluded from p. 289).

Ammonia-gas, when dissolved in water, causes the evolution of much heat. Yet a stream of this gas directed upon the jet has no action. [Experiment.]

Ozonised air, which Mascart found so effective in his experiments with the closed vessel, is quite inoperative with the steam jet. Equally so is the vapour of boiling formic acid, which I believe is chemically a much more active acid than acetic, and has a lower electrical resistance. (See Table).

### *Condensation of Steam Jet.*

*Active.*

Air, oxygen or nitrogen, in which electrical discharge is occurring.

Burning and incandescent substances.
Fumes from phosphorus.
Hydrochloric acid.
Sulphuric acid vapour.
Nitric acid vapour.
Acetic acid vapour.

*Inactive.*

Air, &c., in which electrical discharge has ceased for about ten seconds.

Smoke without fire.
Bottled phosphorus fumes.
Ammonia.
Ozone.
Steam.
Alcohol vapour.
Formic acid vapour.
Sulphurous acid.

It seems that we have here a pretty little problem which might, perhaps, be solved without much difficulty by a competent chemist, but which quite baffles me.* Is it possible that the condensing vapours may contain dissociated atoms?

To return to the electrical effect. There are only two kinds of chemical change that I know of which could be brought about in air by an electrical discharge. Either some of the oxygen might be converted into ozone, or the oxygen and nitrogen of the air might be caused to combine, forming nitric acid or some such compound. The former of these would not account for the action of the air upon the jet, because, as we have seen, ozone is inoperative; the latter might. But if the activity of the air is due to the presence in it of a compound of oxygen and nitrogen, then it is clear that an electrical discharge in either nitrogen or oxygen separately would fail to render those gases active.

I arranged a spark bottle, inside which an induction-coil discharge could be made to take place; two bent tubes were passed through the cork, one reaching nearly to the bottom for the ingress of the gas to be tested; the other, a shorter one, for its egress. The open end of the egress tube was fixed near the steam jet, and first common air, then oxygen, and then nitrogen were successively forced through the bottle while the coil discharge was going on. All produced dense condensation, but I thought that oxygen appeared to be a little more efficient than common air, and nitrogen a little less.

This last experiment points to a conclusion to which at present I see no alternative. It is that the action on the jet of an electrical discharge is due in some way or other to dissociated atoms of oxygen and nitrogen. There is nothing else left to which it *can* be due.

So far as Robert Helmholtz's explanation coincides with this conclusion I think it must be accepted as correct. As to the precise manner in which he supposed the dissociated atoms to act upon the jet, it is more difficult to agree with him. He thought that the abnormal condensation was a consequence of the molecular shock caused by the violent re-combination of the dissociated atoms in the supersaturated air of the jet, the action being analogous to that which occurs when a supersaturated solution of sulphate of soda, for example, is instantly crystallised by a mechanical shock.

To me this hypothesis, ingenious as it is, seems to be more fanciful than probable, but I can only hint very diffidently at an alternative one. To many chemical processes the presence of water is favourable, or even essential. Is it possible that the re-combination of free atoms may be assisted by water? And is it possible that dissociated atoms in an atmosphere of aqueous vapour may obtain the water needed for their union by condensing it from the vapour?

According to Helmholtz, flames and incandescent substances generally cause dissociation of the molecules of oxygen and nitrogen in the surrounding air. This, I believe, is generally admitted. I do not know whether slowly oxidising phosphorus has the same effect.

If it is conceded that the atmospheric gases are dissociated by electrical discharges, and that the presence of such dissociated gases somehow brings about the dense condensation of water vapour, we may still regard the electrified steam jet as affording an illustration of the abnormal darkness of thunder-clouds.

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* A Lecture delivered at the Royal Institution of Great Britain May 5, 1893.

* Two chemists of the highest eminence have been good enough to consider the problem for me, but they are unable to throw any light upon it.

Perhaps another source of dissociated atoms is to be found in the ozone which is generated by lightning flashes. A molecule of ozone consists of three atoms of atomic oxygen, while one of ordinary oxygen contains only two. Ozone is an unstable kind of material and gradually relapses into ordinary oxygen, the process being that one atom is dropped from the three atom molecules of ozone, these detached atoms in course of time uniting with one another to form pairs. Thus two molecules of ozone are transformed into three of oxygen. A body of ozone is therefore always attended by a number of dissociated atoms which are looking for partners.

In the steam jet experiment there is not time for the disengagement of a sufficient number of isolated atoms from a blast of ozone to produce any sensible effect. But the case is otherwise when the vapour is confined in a closed vessel, as in Mascart's experiment, or when it occurs in the clouds, where the movement of air and vapour is comparatively slow.

Ozone, it will be remembered, was found by Mascart to produce dense condensation in a closed vessel even after being filtered through cotton-wool. Similar filtration seems to entirely deprive the so-called products of combustion of their active property, a fact which has been adduced as affording overwhelming evidence in favour of the dust nucleus theory. Coulier himself, however, detected a weak point in this argument. He produced a flame which could not possibly have contained any products of combustion except steam, by burning pure filtered hydrogen in filtered air; yet this product was found to be perfectly capable of causing dense condensation, and, as in his former experiments, filtration through cotton-wool deprived it of its activity.

These anomalies may, I think, be to a great extent cleared up if we assume that the effect of the cotton-wool depends, not upon the mere mechanical obstruction it offers to the passage of particles of matter, but upon the moisture which it certainly contains, and which may act by attracting and facilitating the reunion of dissociated atoms before they reach the air inside the vessel. According to this view ozone would remain an active condenser in spite of its filtration, because free atoms would continue to be given off by it after it had passed the cotton-wool. The filtration experiment should be tried with perfectly dry cotton-wool, which, however, will not be easily procured, and, if my suggestion is right, dry wool will be found not to deprive ordinary products of combustion of their condensing power.

To sum up. I think my recent experiments show conclusively that the dense condensation of the steam jet is not due directly either to electrical action or to dust nuclei. The immediate cause is probably to be found in dissociated atoms of atmospheric gases, though as to how those act we can only form a vague guess.

The discourse concluded with some remarks upon atmospheric electricity, and the exhibition of lantern photographs of lightning flashes.

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## ON THE PHOTOGRAPHY OF THE LUMINOUS RAYS OF THE SHORTEST WAVE-LENGTHS.*

By VICTOR SCHUMANN, of Leipzic.

(Continued from p. 290).

D. *In Air.*—In my previous proofs of the most refrangible rays a reduction of the focal distance had reduced the resistance of the air to the desired degree. The present purpose required more energetic means. The air must be removed entirely, or at least so far that its resistance did not permanently damage the photographic effect. The conditions were therefore again pressing, but this time for photographing in a vacuum to a heightened extent, which my former designs for a spectral apparatus translucent for the ultra-violet had already taken into consideration.

Still the same considerations as formerly stood in the way of the execution of an exhausted spectroscope. And yet it was the sole remaining means that offered a prospect of success as long as I would not forsake the systematic examination of the obstacles.

The technical difficulties in the construction of such an apparatus were increased as soon as we wished to place in the vacuum not merely the prism and the lenses, but also the plate and the slit. If both remain outside the vacuum, not merely the construction of the apparatus but also its management will be much simplified. The adjustment of the slit, the care of its edges, the exchange of the plates, and the displacement of the case in series of proofs, as well as the arrangement of the case itself, can remain exactly as in an ordinary spectral apparatus.

The exhaustion may then be effected more simply. It does not need to take place at every change of the plates. The apparatus when once exhausted is available for a long time and for any desired number of proofs. At the same time such an instrument is relatively simple in its exhausted part, and the stratum of air between the slit and the plate can be brought without difficulty to the modest dimension of 1 centimetre in thickness.

According to the observations of others as well as to my own I considered a stratum of air of this thickness as quite unobjectionable for the present purpose. If the air had been at all an obstacle in my earlier proofs with a short focal distance the spectrum must decide when I reduced the thickness of the stratum to more than its thirtieth part, as was actually the case in a stratum of air of the thickness of a centimetre.

This idea was at the foundation of the apparatus with which I sought to decide on the absorption of the most refrangible rays in the air.

I introduced the prism and the lenses of the apparatus of a short focus, carefully observing their respective positions, into a brass case closed air-tight. It had behind the slit and in front of the photographic plate two apertures for light, which were closed with plane parallel plates of fluor-spar. Without the vacuum, at the distance of 2 m.m. vertically from the fluor-spar plate concerned, were the aperture of the slit and the photographic plate. When in use the apparatus was connected (by means of a glass ground junction) with a mercurial air-pump (Geissler, of Bonn), by which it was exhausted according to the manner of Geissler tubes.

This was, in broad outlines, my first exhaustible spectrum apparatus. I omit here a minute description of the movement of the object lens, the slide of the slit, and the track of the case, as I purpose mentioning them in full by the opportunity of certain important improvements which I devised afterwards. But for the better understanding of the following results I will describe the path of the rays between the spark and the photographic plate at the respective distance of 4 m.m. The rays traversed before reaching the vacuum a stratum of air of 6 m.m. in thickness and the first closing plate (3 m.m.), in the vacuum the lens of the collimator, the prism, and the lens of the camera, on leaving the vacuum at the angle of 20° the other closing plate of the same thickness, and lastly, still at the same angle, the stratum of air of 2 m.m. which separated the covering plate from the photographic plate. As the prism of the lenses were of fluor-spar no other absorbents came into consideration except air, which acted as a stratum of approximately 10 m.m. in thickness.

The spark was supplied by the smaller inductorium and a Leyden jar. The electrodes were of aluminium and tungsten. The photographic plates were by Schleussner. Their treatment was like that already described.

(To be continued).

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* From the Reports of the Session of the Imperial Academy of Sciences at Vienna (*Mathemat.-Natur. Class.*, vol. cii., Part II., April, 1893).

## ON THE ASSAY OF THE MANGANESE OXIDES BY MEANS OF HYDROGEN PEROXIDE.

By ADOLPHE CARNOT.

It is known that oxygenated water is decomposed with effervescence in contact with manganese peroxide, and that a small quantity of this oxide is sufficient to destroy an indefinite quantity of oxygenated water.

It is not the same when the peroxide and the oxygenated water are in contact with an acid, even if very dilute or feeble, capable of combining with manganese oxide. There is then a simultaneous decomposition of the two peroxides, and the quantity of oxygen evolved is exactly double of that found in manganese peroxide in excess of MnO.

This reaction is produced readily even in the cold with nitric acid. The author's method agrees in principle with that of Dr. Lunge, but the arrangement is different, no special apparatus being required. Carnot makes use of a small flask, holding about 150 c.c., closed with a caoutchouc stopper, having two perforations. In one of these passes a straight tube, drawn out at the lower end and fitted at the top with a funnel and a glass cock. The other admits the delivery-tube, bent in the shape of S, and terminating at the top of a graduated jar, containing 300 c.c., filled with water, and placed over a water trough.

We put into the flask 1 grm. of the oxide to be examined, then about 30 c.c. of water, and 20 c.c. of nitric acid, in order to decompose any nitrates which the ore may contain. When all carbonic acid has been expelled we insert the stopper, but without introducing the drawn-out tube tube as far as the liquid We leave the cock open and introduce the delivery-tube under the graduated jar. The tube is then filled with water as far as its issue from the water trough.

The flask is fixed on a stand with clasps. The tube is immersed to the bottom of the flask, the glass cock is closed, and we pour into the funnel 20 c.c. of oxygenated water at 10 vols. Carefully turning the cock, we allow the reagent to flow gently into the flask, and we close the flask at the moment when the last portions of the liquid have passed through. With most manganese oxides the reaction takes place at once, without heating, and is completed in a few minutes if we take care to shake the flask from time to time. For some very compact oxides it is necessary to heat slightly to complete the reaction. It is then necessary to cool the flask, or give it time to return to the temperature of the external air, before proceeding to measure the gas.

It is sufficient to measure the increase of the total gaseous volume, taking care that the temperature and the pressure have remained the same as at the beginning of the experiment. For this purpose the graduated jar is grasped in wooden tongs or with a layer of paper to prevent the direct contact of the fingers, and it is lowered into the water trough until the level of the water is exactly the same within and without. The branch of the S-tube which had been inserted in the graduated jar is withdrawn. The jar is immersed into the water to give the gas which it contains the temperature shown by the thermometer inserted in the water trough, and we determine the volume of the gas after having brought it to the atmospheric pressure.

Let V be the volume thus found. In order to have the total gaseous volume, it is necessary to add to V the small volume, $v$, of gas which has filled the extremity of the delivery-tube, originally full of water, a volume which is easily measured once for all. On the other hand, we must deduct the volume of oxygenated water which has been introduced into the flask, and which has displaced an equal volume of gas. This volume equals 20 c.c. We represent the total increase of the gaseous volume by $V t$; that is to say, $V + v = 20$ c c. The valuation has been made at the temperature, $t$, and the atmospheric pressure, H, observed in the experiment. The gas is saturated with moisture, the tension of which is known, according to the temperature. As this increase is due to the oxygen yielded, half by the manganese oxide, and half by the oxygenated water, we must only take the half to calculate the gas yielded by 1 grm. of the ore.—*Bull. de la Soc. Chim. de Paris.*

## METHOD FOR THE BACTERIOLOGICAL EXAMINATION OF WATER.

By Dr. G. P. DROSSBACH.

The present universally received method for the bacteriological examination of water, which consists essentially in the distillation of a measured quantity of water in nutrient gelatin and the enumeration of the colonies visible with the lens which have grown up in two or three days, has scarcely more than a relative value, which falls more into the rear if the investigation is made, not for technical, but for dietetic purposes. According to our present knowledge of the vital conditions of pathogenous microbia it cannot be expected that they can be brought to development in the above-mentioned manner. Even such pathogenic species as flourish relatively well on our artificial nutrient media at a moderate temperature do not reach this characteristic development in less than three or four days. But in the same time the saprophytes and hyphomycetes, which are always present in water rapidly liquefy and overgrow the plate. In this manner we therefore detect merely the saprophytes and hyphomycetes as the pathogenic species are not developed during the short time of the experiment.

If the too rapid growth of the colonies is checked by spotting with solution of mercuric chloride, there often appear in from three to five days, mostly in the depth of the gelatin, a great number of colonies belonging to almost all the species which are able to grow at the temperature of the blood, and which consequently fulfil one condition for developing a pathogenic activity. This customary plate method should only be used for technical purposes or for checking water-filters. For determining the absolute values of a drinking water it is worthless. For such purposes the determination of the germs capable of development at blood-heat, especially those of the optionally anærobic species, is exclusively suitable. That the casting of agar plates requires rather more skill should scarcely be a reason why the last-named process has not been universally introduced. Probably the decisive point has been that to many persons the evacuation of the air and working with Gruber tubes appears too tedious, whilst working with pyrogallol is unpleasant and often unsuccessful.

In order to overcome these difficulties, I examined the properties of other chemicals which absorb oxygen. Ferrous oxide proved to be very useful. Though not capable of giving vital conditions suitable for the most rigidly anærobic species, it suffices for the development of many, and prevents them from being overpowered by the aërobic species. Ferrous oxide is best used in a box-exsiccator, the bottom of which is covered with a layer of concentrated soda lye of 1 to 2 c.m. in depth. This is cautiously superstratified with the concentrated solution of an equivalent quantity of ferrous chloride so that the two liquids do not mix. The lid is put on, and luted with a melted mixture of two parts wax and one part oil of almonds. The liquids are then mixed by means of a rather vigorous circular movement, when the ferrous oxide is set free with a strong production of heat, and coats the interior surface of the exsiccator in the state of a thick paste. If on use the box is not opened longer than it is absolutely necessary, and if a sufficient quantity of oxide is present, the box may be used repeatedly.

Chromous oxide absorbs oxygen much more energetically than ferrous oxide. Chromous oxide, indeed, cannot be used as such, since it decomposes water, and the liberation of oxygen raises the lid of the exsiccator. Chromous acetate may be conveniently used. A concentrated solution of crude chromium sesquioxide is reduced by means of zinc and a little hydrochloric acid until the solution appears of a pure blue. It is poured (without filtration) upon the stratum of soda-lye in the exsiccator, proceeding exactly as directed above. The red acetate liberated absorbs oxygen with extreme energy, the heat liberated reaching even to redness. If the lower part of the exsiccator is of a sufficient size, and from 100 to 200 grms. of chromous chloride have been employed, the box may be used many times in succession.

The most strictly anærobic species are thus developed on the nutrient medium cast in Petri capsules.

It is advantageous not to cover the capsules, and to place them upon each other supported on wire triangles. —*Chemiker Zeitung*.

## INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

### UNDER THE PATRONAGE OF THE BELGIAN GOVERNMENT.

This Congress, which is to be held at Brussels on the 4th of August, 1894, and will last a week, is promoted by the Belgian Association of Chemists, and will have for Honorary President M. de Bruyer, Minister of Agriculture, Industry, and Public Works.

The science and practice of chemical analysis plays such an important part in the commercial side of industrial and agricultural chemistry, both in the control of manufactures themselves and in the solution of hygienic problems, &c., that it becomes more and more important that there should be greater agreement, and accord, between the various methods of analysis now in vogue among analytical chemists. That there should be so much disagreement between the results obtained from different laboratories is greatly to be regretted; but these disagreements (when they occur) are more often caused by the employment of different methods than by any want of skill or care on the part of the operators. To remedy this state of things the Organising Committee of the Congress considers that it is indispensable that there should be a unification of methods of analysis, not only in each country, but universally, and that the standard processes to be adopted should be decided by international agreement. It is in the endeavour to solve the inevitable difficulties of such a scheme that the proposed Congress has been convened.

The Congress will be very much on the lines of the British Association, even to the organisation of excursions to various industrial and agricultural establishments.

The Congress will be divided into four sections:—

A. *Sugar Industries:* subdivided into ten heads, comprising the estimation of water in sugar, the estimation of the commercial value of molasses, the estimation and comparison of colour in sugars, &c.

B. *Agricultural Chemistry:* subdivided into nine heads, comprising the estimation of nitrogen in manures, the complete analysis of Chili saltpetre, the estimation of phosphoric acid, the analysis of milk, &c.

C. *Food Products and Public Health;* subdivided into five heads, comprising the estimation of the purity of butter, distilled liquors, the bacteriological examination of potable waters, the micrographic examination of pepper, &c.

D. *Chemical Biology:* subdivided into seven heads, comprising various problems in brewing, the manufacture of vinegar, the analyses of molasses with regard to distilling, &c.

It is proposed to start eventually a "Review of Reviews of Applied Biological Chemistry," published in several languages, and containing a *résumé* of chemical work of this description from all parts of the world.

We may add that the date of this Congress has been fixed so as to coincide with several *fêtes*, in connection with the universal exhibition to be held at Anvers, so that profit and pleasure may be combined.

Further information with regard to rules, regulations, subscriptions, &c., can be obtained from the Secretary-General, M. Sachs, 68, Rue d'Allemagne, Brussels; or from M. H. van Laer, 15, Rue de Hollande, Brussels.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Ordinary Meeting, December 7th,* 1893.

Dr. Armstrong, President, in the Chair.

Messrs. E. A. Hancock and E. A. Warmington were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Purefoy Fitz-Gerald, Wellington College, Berks; Alfred Hutchinson, The Leys, Cambridge; Frank Hughes, 27, Fairfield Rd., Chelmsford; Norman Leonard, 2*a*, Lorne Road, Brixton, S.W.; Arthur Luty, 30, Bryn-y-Mor Terrace, Swansea; A. H. Macdonald, The Green, Marlborough, Wilts; David Paterson, Lea Bank, Roslin, N.B.; J. Cardwell Quinn, Woodcroft, Gateacre, near Liverpool; Arthur Ross, 1, Glengall Rd., Old Kent Rd., S.E.; Walter Smithson Rowntree, 53, Grosvenor Road, London, S.W.; Richard A. Rouillard, 5, Dundonald Rd., Wimbledon, and Mauritius; Charles Henry Smith, Re Bungalow, Nassau, Bahamas, W.I.; Alfred E. Tanner, 2, Bruce Grove, Tottenham; Hamilton Marc Wingate, 3, Buckingham Street, Glasgow, W.

The following were duly elected Fellows of the Society:—Frederic Edmund Bowman; Harry Fielden Briggs; Frank Browne; John Dixon Brunton; C. M. Caines; Thomas Petson Carswell; Harry J. Chaney; Allan Thomas Cocking; John A. Craw; Charles Sordes Ellis; Alexander M. Forrester; Henry Garnett; W. H. Grieve; Harry Edwin Hadley; Henry Ormsby Hale; Harold Harris; Wm. Hesketh; H. B. Holthouse; Bertram Hunt; W. F. Mawer; J. R. Morgan; F. Morton; George F. Payne; G. P. Rees; Thomas Anderson Reid; Philip Schidrowitz; W. Edgar Sims; Frederick Shapley; Robert Curley Styles; Jocelyn Field Thorpe; William Herbert Walden; Frank Ernest Welchman; William Gilchrist White; Edward Humphreys Winder; Stanley Wyndham.

Of the following papers those marked * were read:—

*84. "*An Apparatus for the Extraction and Estimation of the Gases Dissolved in Water.*" By E. B. Truman, M.D.

The apparatus described is so constructed that the air having been removed chiefly by means of a water pump and ultimately by a Sprengel mercury pump, a measured bulk of the water can then be introduced, if desirable without allowing it to come into contact with the air. The dissolved gases which spontaneously escape from the water can be pumped off, and the water can be subsequently heated so as to drive off any gas remaining dissolved and also the carbon dioxide fixed by carbonates.

*85. "*The Magnetic Rotation of Hydrogen Chloride in Different Solvents, and also of Sodium Chloride and of Chlorine.*" By W. H. Perkin, Ph.D., F.R.S.

Experiments are described which have afforded results confirmatory of those previously published by the author. It is shown that when isoamylic oxide is nearly saturated with hydrogen chloride at temperatures between 0° and 25°, no appreciable interaction takes place, the values obtained by direct weighing agreeing with those afforded by titration with alkali; action takes place only very slowly between the two substances at ordinary temperatures. Hydrogen bromide acts far more rapidly on isoamylic oxide. It is further shown that hydrogen chloride acts extremely slowly on ethylic and isoamylic alcohols at ordinary temperatures. Hydrogen chloride when dissolved in these alcohols has a higher molecular rotation than when dissolved in isoamylic oxide, the value being, however, than that afforded by aqueous solutions, thus:—

| | |
|---|---|
| In aqueous solution .. .. .. | 4·300 |
| In alcoholic solution .. .. .. | 3·324 |
| In isoamylic oxide .. .. .. | 2·245 |

The molecular magnetic rotation of sodium chloride was found to be 4·080 in the solid state and 5·068 in aqueous solution.

The value obtained for chlorine, using a solution in carbon tetrachloride, was 2·188, which is considerably higher than the value calculated from compounds such as propyl chloride (1·733).

*86. "*Analysis of Water from the Zem-Zem Well in Mecca.*" By C. A. Mitchell, B.A. (Oxon.), King's College, London.

Through the kindness of Lady Burton I have been enabled to make an analysis of water from the Zem-Zem well in Mecca, which was obtained from the well by the late Sir Richard Burton, disguised as a pilgrim dervish, in 1853.

The Zem-Zem well, according to tradition, is the well of Hagar, and is used for no other purpose than for drinking and religious ablution. Each pilgrim to Mecca is anxious to drink and bathe in the water, but as there is not sufficient for all the following device is adopted:—An Arab standing on the wall of the well draws the water up and pours it over the pilgrims as, stripped to the waist, they advance in turn. As it pours over him each drinks what he can, and the remainder runs down, soaking through the loin cloth, back into the well to be used again on succeeding pilgrims. If this practice has been continued day after day and year after year, it is not surprising to find that the water is very rich in chlorine and albumenoid ammonia, and that the solid residue is large in amount.

The sample examined was contained in two small hermetically sealed tin bottles, which had remained untouched since Sir Richard Burton brought them from Mecca. Each held about 200 c.c. On opening them there was a slight evolution of gas. In each case there were minute silky crystals in suspension, and a few earthy particles settled at the bottom. These crystals, on examination, proved to be a tin compound, probably stannic hydrate, as they were unaltered on evaporating with strong nitric acid, and, after fusing them with pure sodium carbonate, no trace of chloride or sulphate could be detected in the solution. These foreign matters being filtered off, a clear and colourless filtrate was left, having a slight smell, more perceptible on warming, and distinctly alkaline to litmus paper. Neither tin nor lead was found in this solution. The relative density of the water at 14° was 1·0029. On analysis the following numbers were obtained:—

| | | |
|---|---|---|
| Nitrogen from nitrates and nitrites .. .. .. .. | 4·496 | grs. per gallon. |
| Total solids.. .. .. .. | 219·5 | ,, ,, |
| Chlorine .. .. .. .. | 69·3 | ,, ,, |
| Free and saline $NH_3$.. .. | 71·4 | parts per million. |
| Albumenoid $NH_3$ .. .. | 2·2 | ,, ,, |
| Hardness in terms of $MgCO_3$ .. .. .. .. | 23·3 | |

The hardness in degrees of $CaCO_3 = 43·05$, but as the water was found to contain very little calcium and large quantities of magnesium, the hardness is given in terms of the latter, although probably it is mainly due to chlorides and sulphates.

The oxidised nitrogen present, determined by Lunge's nitrometer, was 4·496 grains per gallon = 19·91 grains $NO_3$.

On igniting the residue, white fumes from ammonium salts were given off, while the residue browned considerably and lost in weight an amount corresponding to 35·5 grains per gallon.

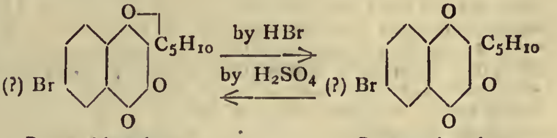
The following are the quantities of some of the constituents of the water actually determined and calculated on 219·5 grains of total solids to the gallon.

| | |
|---|---|
| $SiO_2$.. .. .. .. .. | 3·0 |
| Al .. .. .. .. .. | 0·8 |
| Ca .. .. .. .. .. | 0·5 |
| Mg .. .. .. .. .. | 6·6 |
| K .. .. .. .. .. | 24·3 |
| Na .. .. .. .. .. | 38·3 |
| $NH_4$ .. .. .. .. | 5·3 |
| Cl .. .. .. .. .. | 69·3 |
| $SO_4$.. .. .. .. .. | 30·7 |
| $NO_3$.. .. .. .. .. | 19·9 |

Professor Crookshank was kind enough to make an exhaustive bacteriological examination of some of the water, but was unable to discover any trace of living organisms. The water was sterile, as might well be expected, after its having been hermetically sealed and in total darkness during forty years.

87. "*The Preparation and Properties of Bromolapachol.*" By Samuel C. Hooker.

The author shows that although bromolapachol cannot be prepared by the direct action of bromine on lapachol, it is readily obtained by reducing dibromolapachone, the preparation of which he has previously described (*Trans.*, 1893, 424). Bromolapachol crystallises in golden scales melting at 170—171°; it yields bromo-β-lapachone when dissolved in concentrated sulphuric acid. Bromo-β-lapachone closely resembles lapachone in its behaviour, being converted into bromo-α-lapachone by the action of bromhydric acid; the latter compound being re-converted into the former by dissolving it in concentrated sulphuric acid. Bromo-α-lapachone is a pale yellow substance melting at 178°; the isomeric *p*-compound is orange-red, and melts at about 205°.



Bromo-β-lapachone. Bromo-α-lapachone.

88. "*Studies on Citrazinic Acid.*" Part II. By T. H. Easterfield and W. J. Sell.

The authors find that when diammonic citrate is heated during several hours at 130° in an open vessel, about 6 per cent of citrazinic acid is produced. The ethylic salt of citrazinic acid yields the ammonium salt of citrazinamide when heated in a sealed tube with strong ammonia. Sodium amalgam reduces citrazinamide,—

$$C_5H_4NO_2{\cdot}CONH_2,$$

to citrazinyl alcohol, $C_5H_4NO_2{\cdot}CH_2OH$, a small quantity of the corresponding hydrobenzoin being simultaneously produced; this behaviour is analogous to that of the amides of aromatic acids. The alcohol crystallises from water in monohydrated colourless prisms, melting at 158°; its solution is very acid to litmus.

89. "*The Oxides of the Elements and the Periodic Law.*" By R. M. Deeley.

The author discusses the properties of the oxides of the elements in connection with the modified periodic arrangement of the elements described in his previous communication (*Trans.*, June, 1893).

In the diagram which accompanied that paper, the "volume heats" and "volume atoms" of the elements were plotted as ordinates, the abscissæ being the atomic weights. Similarly a diagram has now been prepared, in which the ordinates are numbers obtained by dividing the relative densities of the oxides by the atomic weights of the corresponding elements. The results obtained are, in general, confirmatory of those deduced from the previous diagram, and lead to a somewhat similar periodic table, although the arrangement differs in several important respects from that proposed by Mendeleeff.

90. "*The Freezing-points of Alloys in which the Solvent is Thallium.*" By C. T. Heycock and F. H. Neville.

The addition of lead to thallium raises the freezing-point. The atomic falls caused by gold, silver, and platinum in thallium are closely accordant, the mean value being 6·31° as that due to 1 atomic proportion dissolving in 100 atomic proportions of thallium; with the aid of this value, the latent heat of fusion of 1 grm. of thallium is calculated to be 5·12 calories. Bismuth exhibits the phenomena of a triple alloy, probably owing to the presence of impurity in the thallium.

## PHYSICAL SOCIETY.

*Ordinary Meeting, December 8th, 1893.*

Prof. A. W. Rücker, M.A., F.R.S., President, in the Chair.

Messrs. J. H. Gillett and F. Hovenden were elected Members of the Society.

A paper by Mr. James Swinburne on "*A Potentiometer for Alternating Currents*" was read by Mr. Blakesley.

After referring to the many advantages of the "potentiometer method" of measurement, the author describes an arrangement by which alternating pressures can be measured. A quadrant electrometer with a double fishtail-shaped needle suspended by a torsionless fibre is employed. The electrostatic attraction exerted by an alternating pressure between the needle and one pair of quadrants is balanced by the force due to a steady pressure between the needle and the other pair of quadrants. The magnitude of the steady pressure is determined by a potentiometer and standard cell, and the effective value of the alternating pressure thus deduced. For measuring alternating currents a differential electrodynamometer having two fixed coils and one moving coil and no controlling spring is used. A direct current, measured by the fall of potential over a small resistance, is passed through one of the fixed coils, the alternating current through the other fixed coil, and the moving coil is included in both alternating and direct current circuits. When the two forces balance, the currents are taken as equal. Several small inaccuracies to which the method is subject are mentioned in the paper.

Prof. S. P. Thompson enquired if the fishtail-shaped needle of the electrometer was novel.

Mr. Blakesley said the author had mentioned the needle previously. He (Mr. Blakesley) thought the name "potentiometer" was not very suitable. In effect the so-called measurement of *pressures* was a comparison of two *powers*.

The President announced that Mr. Preece's note on the "Specific Resistance of Sea-water" had been temporarily withdrawn.

Prof. G. M. Minchin, M.A., made a communication on the "*Calculation of the Coefficient of Self-induction of a Circular Current of given Aperture and Cross-section.*"

Instead of assuming the cross-section of the wire small and the current density constant over the section, as is usually done, the author takes into account the dimensions of the section and the non-uniform distribution of the current. Making use of the expressions for the vector potential (G) of the current given in his previous papers (*Phil. Mag.*, April and August, 1893), the author calculates the total normal flux of force through a surface intersected once in the positive direction by every tube of force emanating from the given current. This flux, divided by the current, gives the coefficient of self-induction. The surface chosen is the circular aperture of the current and half of the anchor ring formed by the wire. When the current density is inversely proportional to the distance from the axis of the circular current, the value for the coefficient of self-induction is found to be—

$$\pi\left\{4a(\mathrm{L}-2)+2c\left(\mathrm{L}-\frac{5}{4}\right)-\frac{c^2}{16a}(2\mathrm{L}+19)\right\},$$

where $a$ is the radius of the central filament of the current, $c$ the radius of the cross section of the wire, and—

$$\lambda/e\left[\log._e\frac{\delta a}{c}\right].$$

Clerk-Maxwell's approximate expression agrees with this in the principal term. As an example of the closeness of the approximation, the case of a current in a wire 2 m.m. diameter bent to a circle of 2 c.m. mean diameter had been taken, the approximate and corrected coefficients being 58·866 and 59·207 absolute units respectively. When the current in the wire is superficial, as in case of alternating currents of high frequency, the coefficient is somewhat greater, being given by the expression—

$$\pi\left\{4a(\mathrm{L}-2)+2c\left(\mathrm{L}+\frac{3}{2}\right)+\frac{c^2}{16a}(4\mathrm{L}+11)\right\}.$$

Incidentally it was pointed out that the function G.$x$, where G is the vector potential at a point distance $x$ from the axis of a circular current, was the same as Stoke's *current function* in hydrodynamics.

Another paper on the "*Magnetic Field of a Current Running in a Cylindrical Coil*" was read by Professor Minchin.

The cylindrical coil is regarded as a series of equal circles lying close together and forming a cylindrical surface. Replacing each circular current by its equivalent magnetic shell, the problem of finding the magnetic potential at a point resolves itself into calculating the gravitational potential due to two circular plates of attracting matter, one positive and the other negative, situated respectively at opposite ends of the cylinder. The magnetic potential due to one plate is then deduced in terms of elliptic integrals of the first, second, and third kinds. The President had pointed out that the expressions given in the printed proof of the paper only applied when the perpendicular from the point to the plate fell within the circle; the author had therefore modified the formula so as to be true generally. From this formula the equipotential curves can be constructed. The same system of curves serve for the plate at the other end of the cylinder by changing the signs of the numerals representing the potentials, and giving the curves a motion of translation equal to the length of the cylinder in the direction of its axis. The equipotential curves for the coil can then be deduced by drawing through the points of intersection of the two sets of curves whose numerical values have a constant sum. In determining the curves the author had to calculate tables of elliptic integrals of the third kind, and these he hoped to complete before the paper was published.

In reply to a question on the first paper which had been brought before him by Prof. Perry, the author said that as the diameter of the wire diminished indefinitely, both the self-induction and resistance became infinite, but the ratio L/R became zero. It was interesting to examine what relation between the aperture and cross section gave minimum impedance. If the ordinary expression for L be taken, the problem was impossible, but the corrected form admitted of a solution.

Prof. **Perry** hoped the work Prof. Minchin had done so well for circles and cylinders would be extended to cylindrical coils of rectangular cross-section. It was most important to be able to find the shape of the field produced by such coils.

Prof. S. P. **Thompson** enquired if there was any way of deducing the expression for the magnetic force at a point other than that given in the paper on the "Magnetic Field of a Circular Current" (*Phil. Mag.*, April, 1893).

In reply, Prof. **Minchin** explained how the formula followed at once from the fundamental theorem that magnetic force is the curl of the vector potential. This was based on Laplace's expression for the force between a magnetic pole and an element of current, which had been proved experimentally.

## ROYAL INSTITUTION OF GREAT BRITAIN.

*Special General Meeting, Friday, December* 15, 1893.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following Resolution, in reference to the decease of Dr. John Tyndall, Honorary Professor of Natural Philosophy of the Institution, was read and unanimously adopted:—

Resolved, That the Members of the Royal Institution of Great Britain, in Special General Meeting assembled, hereby record their deep regret at the death of Dr. John Tyndall, D.C.L., LL.D., F.R.S., who was for forty years connected with the Institution, as Lecturer, Professor, and Honorary Professor of Natural Philosophy, and who, by his brilliant abilities and laborious researches, has nobly promoted the objects of the Institution, and conspicuously enhanced its reputation, while at the same time he extended scientific truth and rendered many new additions to natural knowledge practically available for the service of mankind; and that the Members of the Royal Institution further desire to convey to Mrs. Tyndall an expression of their sincere sympathy and condolence with her in the bereavement she has sustained in the loss of her gifted and distinguished husband.

Letters of regret for non-attendance were read from His Grace the Duke of Northumberland, K.G. (the President), H.R.H. the Count of Paris, the Right Hon. Lord Kelvin, the Right Hon. Lord Rayleigh, Lady Amherst, of Hackney, Lady A. F. Elphinstone, Sir James N. Douglass, Sir William O. Priestley, the Rev. Canon Jenkins, Mr. Joseph Brown, Mr. A. B. Bassett, Professor T. E. Thorpe, Mr. John Bell Sedgwick, and many others.

## CORRESPONDENCE.

### EASY RULES FOR CONVERTING THERMOMETRICAL DEGREES.

*To the Editor of the Chemical News.*

Sir,—I think Mr. Hersey, whose letter appears in Chem. News, vol. lxviii., p. 293, underestimates his own mental powers. The point is simply, *e.g.*, whether it is easier to multiply a number by 5 and divide by 9, or to double it and subtract all but the last figure. None but Mr. Hersey of those to whom I showed it had any doubt about the superiority of the doubling method. The whole matter is perhaps too simple to be worth a discussion, but I think it desirable to employ arithmetical shorthand wherever possible. My method also avoids more than one "remainder" or fraction: the old method, as per Mr. Hersey, would give remainders that would double the time needed, and lead to possible mental errors.—I am, &c.,

G. Watmough Webster.

## NOTICES OF BOOKS.

*Laboratory Teaching, or Progressive Exercises in Practical Chemistry.* By Charles Loudon Bloxam. Edited by A. G. Bloxam, Head of the Chemistry Department, The Goldsmith Institute, New Cross, London. Sixth Edition. London: J. and A. Churchill. 1893. Small 8vo., pp. 324.

Bloxam's "Laboratory Teaching" has been long a favourite both with teachers and students, and we are bound to say with the fullest right. Whilst in the present edition the general character of the book has been preserved, certain additions and modifications have been adopted which will increase its value. Among these improvements may be mentioned schemes and explanatory instructions for the analysis of complex substances. The section on blowpipe analysis has been remodelled and arranged for the same purpose. The detection of organic substances, especially in mixtures, has been facilitated by the introduction of group-tests and instructions for the elimination of substances which, if present, may occasionally mask the reactions of those sought for. For this purpose the scheme given on p. 282, with the succeeding directions, will be found very useful.

Among poisons we note that chromium has been overlooked (p. 391); yet it is decidedly more formidable than copper, and the numerous uses of its compounds in the arts render its accidental presence in articles of food far from improbable. Uranium is so rarely present, except in insoluble colours, that its omission is perfectly justifiable

We cannot doubt but that the present edition will be no less favourably received than its predecessors.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 23, December 4, 1893.

**Assay of the Manganese Oxides by Oxygenated Water.**—Harry C. Jones.—A paper bearing this title has been recently communicated to the Academy by M. Ad. Carnot (*Comptes Rendus*, cxvi., 1295). I request permission of the Academy to point out that the analytical method indicated by M. Carnot is the application of a more general method elaborated by myself about four years ago and published three and a-half years ago or thereabouts. It has long been known that on the contact of the metallic peroxides with hydrogen peroxide there ensues an evolution of oxygen. G. Lunge has shown that in presence of an acid this reaction is effected quantitatively. He has determined manganese peroxide by means of oxygenated water in presence of sulphuric acid. M. Carnot mentions merely the method of A. Riche, who determines oxygenated water by means of manganese peroxide in sulphuric acid. In the method which he proposes the determination of manganese peroxide is effected by means of oxygenated water in presence of nitric acid. Under these conditions the oxygen evolved is derived half from the manganese peroxide and half from the oxygenated water, according to the equation—

$$MnO_2+H_2O_2+2HNO_3 = Mn(NO_3)_2+2H_2O+O_2.$$

If we know the quantity of the substance employed and measure the oxygen evolved a very simple calculation shows the quantity of manganese peroxide. M. Adolphe Carnot shows also that the same method may serve to determine the oxides $Mn_3O_4$ or $Mn_6O_{11}$, and gives us finally to understand that the method may be utilised for the analysis of the ores of manganese. On consulting the *American Chemical Journal* (xii., 279, 1890) it will be seen that this is precisely the method which I have discovered and developed. The same method has been inserted in the *Analyst* (xvi., 215), and an abstract is to found in the *Centralblatt*, Ser. 2, p. 1027, 1890. On the same occasion I showed that minium and lead peroxide may be determined by means of lead peroxide in presence of nitric acid. Half of the oxygen evolved is obtained from the lead oxide and the other half from the oxygenated water. As I mentioned above Prof. Lunge has shown that manganese peroxide may be determined by means of oxygenated water in presence of sulphuric acid. I have pointed out that nitric acid may be used with advantage, as it peroxidises any ferrous oxide found in the ores of manganese and thus prevents any loss of oxygen. I have further shown that we may determine oxygenated water by means of an excess of minium or lead peroxide in presence of nitric acid as well as by Lunge's method, which involves the use of chloride of lime.

**The Complex Acids Formed by Molybdic Acid with Titanic Acid and Zirconia.—E. Péchard.**—If we add hydrofluosilicic acid to a hot solution of ordinary ammonium molybdate the mixture turns yellow, and on cooling deposits a crystalline precipitate if the liquid is sufficiently concentrated. If the liquid is dilute the addition of hydrochloric acid at once causes the formation of the same yellow crystalline precipitate, which is the ammonium silico-molybdate—

$$2(NH_4)_2O.SiO_2.12MoO_3 + Aq.$$

This method of preparing the silico-molybdates has enabled the author to obtain salts containing molybdic acid with titanic acid or zirconia. He describes the ammonium and potassium titano-molybdates, titano-molybdic acid, and the zincono-molybdates. The process enables us to foresee the existence of analogous compounds of molybdic acid with stannic acid and boric acid.

**Researches on the Constitution of the Albumenoids Extracted from the Vegetable Organism.—E. Fleurent.**—It is now established that the animal albumenoids have a different composition from the albumenoids of the vegetable organism. Thus, caseine contains—C, 48·55; H, 8·20; whilst gluten contains—C, 49·70; H, 8·20.

**Stability and Conservation of Dilute Solutions of Mercuric Chloride.—L. Vignon.**—The antiseptic value of the solutions of sublimate is evidently connected with the preservation of their initial state, which varies rapidly with time.

**Detection of Abrastol in Wines.—M. Sanglé Ferrière.**—Abrastol is the sulphuric ether of $\beta$-naphthol combined with calcium, $[C_{10}H_7O(SO_3)_2Ca]$. To detect this compound in wine we take 200 c.c. of wine and add 8 c.c. of hydrochloric acid, and heat for an hour with an ascending condenser. The liquid when cold is exhausted with 50 c.c. of benzene, which is washed and exposed to slow evaporation without any rise of temperature. The residue is then taken up in 10 c.c. of chloroform, which is put in a test-tube into which is dropped a fragment of caustic potash and heated for one or two minutes to the temperature of the ebullition of chloroform, when there appears a fine blue colour, which changes quickly to green and then to yellow. This reaction is sensitive to 1-80,000th, and enables us to detect 0·10 grm. abrastol per litre.

## MEETINGS FOR THE WEEK.

Wednesday, 27th.—British Astronomical, 5.
Thursday, 28th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.
Saturday, 30th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.

THE CHEMICAL NEWS.

Vol. LXVIII., No. 1779.

NOTE ON

## NATIVE COPPER FROM YUNNAN (CHINA).

By W. GOWLAND, Assoc. R.S.M.,
Late of the Imperial Japanese Mint.

The specimen of native copper—the subject of this note—was sent from the province of Yunnan, in China, to the Imperial Mint, Osaka, Japan, to be examined and reported on.

The mineral was obtained from an outcrop, in which it was said to occur in great abundance, and which it was proposed to exploit by western methods. As the occurrence of native copper in this locality has not hitherto been reported, and as the specimen is of great purity, the following brief account of it may be of interest to mineralogists and metallurgists:—

The specimen consisted of a flat nodular nucleus of metallic copper without crystalline structure, which was incrusted with layers of cuprite and green carbonates of copper. Unfortunately no traces of gangue were attached to it, and no specimens of the other materials of the rim or of the "country" rock were received, hence the mineralogical and geological conditions of its occurrence could not be determined.

*Analyses of Native Copper.*

| Locality .. | Chili. | Lake Superior. | Yunnan. | Lake Superior. | Lake Superior. | Brazil. | Ural, Siberia. | Bolivia. | Bolivia. | Bolivia. | Lake Superior. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Analyst .. | Abel.[*] | Abel.[*] | Gowland. | Rammelsberg.[†] | Abel.[*] | Marchand and Scheerer.[‡] | Abel.[*] | Von Bibra.[§] | Von Bibra. | Von Bibra.[§] | Hautefeuille.[†] |
| Copper.. .. .. | — | — | 99·946 | — | — | 99·56 | — | 97·39 | 97·50 | 97·48 | — |
| Silver .. .. .. | min. trace | 0·002 | 0·026 | nil | 0·56 | 0·30 | 0·034 | — | — | — | 7·30 |
| Gold .. .. .. | nil | nil | nil | — | nil | 0·08 | — | — | — | — | — |
| Iron .. .. .. | min. trace | ,, | 0·028 | 0·31 | ,, | 0·10 | — | 1·80 | 2·02 | 2·24 | — |
| Bismuth .. .. | nil | ,, | nil | — | ,, | — | 0·011 | — | — | — | — |
| Arsenic .. .. | ,, | ,, | ,, | — | ,, | — | 1·28 | — | — | — | — |
| Antimony .. .. | ,, | ,, | ,, | — | ,, | — | — | trace | trace | trace | — |
| Tin .. .. .. | ,, | ,, | ,, | — | ,, | — | — | — | — | — | — |
| Lead .. .. .. | ,, | trace | ,, | — | ,, | — | min. trace | — | — | — | — |
| Mercury .. .. | — | — | — | — | — | — | — | — | — | — | 0·03 |
| Nickel and cobalt | — | — | nil | — | — | — | — | — | — | — | — |
| Gangue .. .. | — | — | ,, | — | — | — | — | 0·44 | 0·21 | — | — |
| | | | 100·000 | | | 100·04 | | 99·63 | 99·73 | 99·72 | |

[*] *Journal Chemical Society* (2), i., p. 89.
[†] Rammelsberg. "Handbuch der Mineral Chemie," Art. "Kupfer."
[‡] Percy, "Metallurgy," i., 286.
[§] *Journal fur Prakt. Chemie*, xcvi., 205.

The weight of the metallic portion was 208·6 grms., and of the incrusting material 89·5 grms.

The metal was of extraordinary toughness and could be bent over completely, even when first deeply cut with a chisel, without showing the slightest trace of fracture. A careful analysis was made of the metal after it had been perfectly freed from the incrusting matter. The following results were obtained:—

| | | |
|---|---|---|
| Copper (by diff.) .. | 99·946 | |
| Iron .. .. .. .. | 0·028 | |
| Silver .. .. .. | 0·026 | |
| Gold .. .. .. .. | nil | A special search for these metals was made, but no trace of any were found. |
| Lead .. .. .. .. | ,, | |
| Arsenic .. .. .. | ,, | |
| Antimony.. .. .. | ,, | |
| Bismuth .. .. .. | ,, | |
| Nickel and cobalt .. | ,, | |
| | 100·000 | |

The percentage of copper was not directly determined in it, as, after several volumetric determinations, it was found to be of greater purity than the specimens of electrotype copper which had been supplied to the Mint as especially pure from two different sources.

In the principal works on mineralogy it is generally stated that native copper is usually pure or nearly pure. Dana, in his "System of Mineralogy," qualifies this, saying that "it often contains silver, bismuth, mercury, &c." I have, however, failed to find that these statements of the text-books are based on many exhaustive analyses, and hence append the accompanying Table containing all the analyses of native copper of which I can find any record, including, for the sake of comparison, this specimen from Yunnan.

From these it will be seen that the native copper from Chili and Lake Superior alone—and the latter not always—are of great purity, that this from Yunnan very closely approaches them in purity, and that the other localities given yield an impure mineral containing considerable proportions of one or more metals.

December 19, 1893.

Note.—Since the Table below was in type I have met with another analysis of a specimen, which I append:—

| Locality .. . | Bolivia. |
|---|---|
| Analyst .. | Kroeber.[‖] |
| Copper.. .. .. .. | 98·605 |
| Silver .. .. .. .. | trace |
| Gold .. .. .. .. | — |
| Iron .. .. .. .. | 1·376 (as loss) |
| Bismuth .. .. .. | — |
| Arsenic .. .. .. | — |
| Antimony .. .. .. | — |
| Tin .. .. .. .. | — |
| Lead .. .. .. .. | — |
| Mercury .. .. .. | — |
| Nickel and cobalt .. | — |
| Insoluble .. .. .. | 0·004 |
| Silica .. .. .. .. | 0·015 |
| | 100·000 |

[‖] Bristow, "Glossary of Mineralogy," p. 252.

Medal.—The Bronze Medal of the National Gardeners' Association was unanimously awarded on December 5th to Dr. A. B. Griffiths "for his books on Manures, and for distinguished services rendered to horticultural science."

## PREPARATION OF CUPROUS OXIDE.

By EDWARD J. RUSSELL.

In preparing cuprous oxide by the ordinary method, viz., by reducing $CuSO_4$ with cream of tartar and glucose in presence of excess of alkali, there is sometimes a difficulty in decanting or filtering, especially if we follow the directions given in Watts's "Dictionary," and attempt to "boil until the supernatant liquid is colourless."

The method I have found most convenient is the following modification of a well-known method :—A mixture of $CuSO_4.5H_2O$ with excess of NaCl is dissolved in water and a fairly concentrated solution is obtained. $SO_2$ is now passed through to saturation; the $CuCl_2$ formed, however, instead of being precipitated, remains dissolved in the excess of NaCl. On now heating to expel $SO_2$, we obtain a solution which is either colourless or slightly tinged with green. Solid $Na_2CO_3$ is then added while hot and a beautiful bright red precipitate of $Cu_2O$ obtained. This very speedily settles, and can readily be washed by decantation.

If there is any doubt as to whether the reduction has been completed, a little $Na_2CO_3$ can be added to the solution, and the precipitate thus obtained filtered off; the filtrate will be found to be quite colourless, and can be treated as above described with more $Na_2CO_3$. A quantity of a very pure product can thus be very speedily and easily prepared.

University College of Wales, Aberstwyth.

## ON ENDOTHERMIC DECOMPOSITIONS OBTAINED BY PRESSURE.*

### PART II.—TRANSFORMATIONS OF ENERGY BY SHEARING STRESS.

By M. CAREY LEA.

Of the relations which exist between two forms of energy, mechanical and chemical, very little, if anything, is known. In the second volume of his "Lehrbuch," Ostwald remarks that as to these relations "almost nothing" is known.†

There are certain familiar cases in which mechanical energy may seem at first sight to be converted into chemical energy. The fulminates, iodimide, and other substances explode by shock. But it is hardly necessary to remark that all such reactions are exothermic, and need an external impulse only, to start them—if this impulse were not needed such compounds could not exist at all. Were such reactions taken as true transformations of energy, an absence of due relation between cause and effect would be involved. For the shock that suffices to explode a grain of fulminate will equally explode a ton. The faint spark that will explode a grain of gunpowder will also explode a magazine.

Present opinion holds undoubtedly that no true transformation of mechanical into chemical energy is known. Most text-books do not consider the question at all. But Dr. Horstmann in the volume of theoretical chemistry which forms part of the last German edition of Graham Otto's "Chemistry," discusses the matter. His views are so much to the point that I shall translate a few sentences, putting in italics the statements to which I would specially refer:—

"We must consequently admit that through a rough mechanical attack the molecular structure of certain chemical compounds can be disrupted and destroyed. This will certainly be possible only for compounds in whose molecules the arrangement of the atoms does not correspond to a stable equilibrium and in which therefore the chemical energies themselves are already striving to form simpler and more stable compounds out of the constituents of the existing substance. *For it cannot be admitted that actual chemical changes can be brought about by a mechanical impulse.*" (*L. c.*, p. 350).

In another chapter he says with equal distinctness :—

"*By mechanical means alone no reaction against the force of chemical energy can be brought about.* By a shock or blow the molecular structure of chemical compounds can indeed be so far loosened that free play is given to chemical forces; *but against these forces we cannot by mechanical means separate the atoms nor combine them in a definite way.*" (P. 594).

These expressions of a distinguished chemist will sufficiently indicate what has been up to the present time the opinion of chemists as to the possibility of transforming mechanical energy into chemical.

In the first part of this paper I believe I have been able to show in a qualitative way the production of true endothermic reactions by mechanical force. In the present part I hope to show an increased number of such reactions, and in one case to exhibit actual quantitative results, at least so far as to obtain the product of the transformation in weighable quantities.

In the first part decompositions were described that were brought about by *simple pressure.* Compounds formed by exothermic reactions, and therefore requiring expenditure of energy to break them up, were decomposed. The investigation might probably have been made to include a still larger range of substances. But it was found that the efficiency of pressure was so enormously increased by the addition of shearing motion, that decompositions requiring a force of hundreds of thousands of pounds with pressure alone, could be effected by the mere strength of the hand when shearing stress was used. More than this, decompositions which enormous pressures failed to effect, readily took place under the action of shearing stress.

(It would not have been difficult to obtain much greater pressures than those described in the first part of this paper. This could be effected by means of the differential screw. I had planned for a screw with threads of 40 turns in 10 inches and 39½ turns in 10 inches respectively. The mechanical efficiency of such a screw is that of one having 320 turns to the inch, if such a thing were practicable; at the same time a thoroughly strong construction can be obtained. The massive steel nut to advance ⅛ of an inch would require 40 full turns of this screw. This arrangement compares as follows with that previously employed. In it to cause the vice jaws to approach by 1 inch required that the point of the lever at which the force was applied should pass through a space of 113·1 feet: this relation, 1 inch to 113·1 feet, or 1 : 1357·2, gives the measure of the efficiency of the instrument. With the double screw, on the other hand, to cause the nut to advance ⅛ of an inch the end of the lever (two feet long) must pass through a space of 500 feet, or in the proportion of 1 inch to over three-quarters of a mile. The circumference described by the lever being approximately 12½ feet, and the screw requiring 40 turns to advance the nut ⅛ of an inch, we get the proportion of 1 inch to 4000 feet, or 1 to 48,000, which is the measure of the efficiency of such an instrument. Therefore, supposing two men to pull on the end of the lever, each with a pull of 100 lbs., the pressure exerted on the nut (disregarding loss by friction) would be 9,600,000 lbs., which could be doubled by using a 4-foot lever. Such a combination is quite practicable, the only only real difficulty being to obtain sufficient solidity of construction to resist the strain. I had made drawings for this instrument, but gave it up in consequence of observing the enormously greater efficiency of shearing

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* From the *American Journal of Science*, xlvi., December, 1893.

† "Andererseits ist von der Verhältnis zwischen mechanischer und chemischer Energie, fast nichts bekannt." A few lines below, this remark is repeated with emphasis. "Lehrbuch," 2nd German ed., vol. ii., p. 12.

stress as a means of transforming mechanical into chemical energy).

(I.)

It was mentioned in a previous paper on the decomposition of the silver haloids by mechanical force that when silver chloride was sharply ground for some time in a mortar, both the pestle and mortar became covered with a deep purple varnish of silver photochloride, thus indicating a partial reduction to subchloride. It has since proved that there is no more effectual method than this of applying shearing stress, and that in this way a number of quite stable chemical compounds formed by exothermic reactions can be broken up. The mortar and pestle should be very solid and of unglazed porcelain. With metal, there would be danger of action between the metal and the substance, and with agate mortars sufficient force cannot well be applied. In many cases success depends on the exertion of great pressure on the pestle. It is also absolutely essential that the quantity of material acted upon should be small. When a larger quantity is employed the particles slip or roll over each other, and thus escape the action of the stress. It is no doubt for this reason that the very remarkable results which can be obtained in this way have hitherto escaped attention.

A small quantity, a few decigrms., of the substance having been placed in the mortar, the first thing is to spread it in a thin uniform coat over the bottom and part of the sides. The pestle is then to be rotated with the utmost force that can be exerted.

*Sodium Chloraurate.*—The salts of gold are particularly well adapted to this examination, as the reduction is complete and the gold appears in the metallic state, so that it can be weighed and the exact amount of reduction can be fixed. It will be seen by (3) below that it may amount to as much as over 4 per cent of the gold present.

(1) Two or three decigrms. of chloraurate with a moderate trituration left 1·8 m.grms. of metallic gold. Under the action of the pestle the yellow colour of the salt gradually deepened to an olive shade. When water was poured on, the undecomposed salt dissolved, leaving the gold as a delicate purple powder. The colour of the gold being purple, instead of the more usual brown shade, explains the olive colour just mentioned, yellow and purple combining to form olive.

(2) Half a grm. of the salt was taken. This specimen was more neutral than the preceding, and was therefore more easily reduced. Half an hour's trituration had for effect the reduction of 9·2 m.grms. of gold.

(3) A similar treatment of the same quantity of chloraurate resulted in the separation of 10·5 m.grms. of gold.

These may seem at first somewhat small proportions. But it is to be recollected that the force is necessarily applied at a disadvantage and that the equivalent in work of chemical affinity is always very large. In the present case the figures are as follows:—Thomsen found as the heat equivalent for the combination of gold with chlorine to form auric chloride 28·8 great calories. Taking the atomic weight of gold as 197, we find that one grm. of gold in forming auric chloride disengages 115·7 small calories or water-gram-degrees, whose equivalent, taking Rowland's determination, is 49,288·2 gram-meters, corresponding to $4{\cdot}83 \times 10^9$ ergs or 483 joules.

The small quantity of gold reduced in (3), 10½ milligrms., would by conversion to auric chloride generate 1·215 water-gram-degrees of heat whose equivalent in work is 518 gram-meters. As heat is a degraded form of energy such an actual transformation without loss to a higher form would be impossible. It is more correct to say, therefore, that the amount of energy which would raise 518 grms. to the height of one metre can be transformed into the same amount of heat, 1·215 water-gram-degrees, as is evolved by 10·5 m.gs. of gold by conversion into auric chloride. Consequently this work, 518 gram-meters represents the amount of mechanical energy transformed into chemical energy in operation (3).*

It does not appear that in effecting these reactions and the others which remain to be described, mechanical energy undergoes an intermediate conversion into heat. Rapid movements are not needed, what is required is strong pressure with movement, but this need not be rapid. Nor does the mortar or the pestle become sensibly warm. The operation does not need to be continuous, but may be broken up with any number of intervals. But a decisive conclusion can be drawn from those cases in which decompositions are effected in this way that *cannot be produced by heat.* For example, in the next instance to be mentioned there is a partial reduction of corrosive sublimate to calomel. By heat, corrosive sublimate sublimes unaltered and the same is true of mercurous chloride. The three silver haloids fuse unchanged at a red heat. The same conclusion can be drawn from other reactions.

These results were obtained in an atmosphere absolutely free from dust, so that the reducing action of this substance was completely excluded.

*Mercuric Chloride.*—A specimen which after lightly powdering did not darken in the least with ammonia was triturated in the manner just described with several intervals, in all for 15 minutes. It then became grey in a very striking way when moistened with ammonia.

This is a very interesting reaction. In the first part of this paper it was mentioned that mercuric chloride could be subjected to a pressure of about 70,000 atmospheres absolutely without change. It appears, however, that a pressure amounting to less than a hundred pounds causes decomposition when combined with movement, showing the enormously greater efficiency of shearing stress as compared with simple pressure. Not only this, but, as just mentioned, shearing stress produces decompositions which heat is not competent to effect.

*Mercurous Chloride.*—When calomel was sharply triturated in a mortar it first became yellow and then blackened without difficulty.

*Turpeth Mineral*, $3HgO,SO_3$.—Reduces rather slowly.

*Mercuric Oxychloride*, $2HgO,HgCl_2$, obtained by precipitating corrosive sublimate by potash acid carbonate, exhibited the following reaction. Its brownish purple colour by light grinding became lighter, and then when strong force was used it blackened with remarkable ease.

*Mercuric Iodide* shows a trace of blackening.

*Mercuric Oxide.*—This substance yields much more readily to trituration than to simple pressure. Especially on the sides of the mortar it was quite blackened. The layer of material must be quite thin, otherwise little effect is produced.

*Platinic Chloride.*—Gradually darkened in a very marked way, finally becoming blackish.

*Ammonium Platinichloride* gave same result.

*Silver Tartrate.*—When spread in a very thin skin over the mortar each sharp stroke of the pestle left a black line behind it. This is a strong contrast with the complete resistance of this substance to simple pressure.

*Silver Carbonate.*—Action similar.

*Silver Citrate.*—Blackens very easily.

*Silver Oxalate.*—At least as easily.

*Silver Arsenate.*—Nearly as easily.

*Silver Sulphite.*—Effect visible in five minutes and gradually increasing. Very well marked.

*Silver Salicylate.*—No silver salt appears to be so easily reducible as this. Every sharp stroke of the pestle leaves a brown mark behind it.

*Silver Orthophosphate.*—Affected easily. After the phosphate has been a good deal reduced the unchanged part may be dissolved out with ammonia. The black residue after washing readily dissolves in dilute nitric acid and the solution gives a white cloud with hydrochloric acid.

---

* The amount of energy required would in fact slightly exceed this, as the thermochemical equivalent of formation of sodium chloraurate would slightly exceed that of auric chloride. For the chloraurate I do not find a determination, but preferred to use this salt in the operation as being both more stable and more neutral than auric chloride.

*Potassium Ferridcyanide.*—A crystal of the pure salt sharply ground in a mortar becomes in portions brown and in others blue. The quantity used must, as indeed in all of the above cases, be small—one or two decigrms. If a little distilled water be added an insoluble blue powder is left behind and the solution formed strikes a blue colour when added to one of ferric alum. This indicates that the decomposition is twofold. The experiment is quite a striking one and the result is easily obtained.

(II.)

This form of mechanical force, shearing stress, may be applied to effect endothermic change in other ways. A very simple, and at the same time very efficient, method is that of pressure with a glass rod. Pure strong paper is to be imbued with a solution of the substance, if it is soluble, or if not it is to be made into a paste with water and then applied with a brush. The paper is to be then very thoroughly dried and is to be laid upon a piece of plate glass. Characters are to be marked on it with the end of a glass rod that has been rounded by heat, using as much pressure as is possible without tearing the paper.

More than twenty years ago I was able to show that marks made in this way on sensitive photographic films could be developed, as an invisible image had been impressed. That, however, is a somewhat different matter from actual and visible decomposition following each stroke of the rod, a result which may be obtained with various salts of gold, mercury, silver, and other metals.

*Potassium Ferridcyanide.* — Pure paper was imbued with a dilute solution of this salt. After thorough drying it was laid on a glass plate and marks were made with a glass rod in the manner just described. These marks were immediately visible and when the paper was plunged into dilute solution of ferric ammonia alum or of ferric chloride they became dark blue. It is probable that the decomposition here effected was two-fold (see above).—The *nitroprussides* appear to be much more stable than the ferridcyanides. When sodium nitro-prusside paper was treated with pressure, followed by appropriate reagents, no indications of decomposition were obtained.

*Auric Chloride.*—Paper imbued with a solution of auric chloride and marked in the manner described was thoroughly soaked in water to remove, as far as possible, the rest of the gold salt. The marks were very distinct and gradually gained with time. Colour dark purplish grey.

*Platinic Chloride.*—After drying and marking, the paper was thoroughly soaked in water and dried. The marks were very distinct, of a yellow colour.

*Ammonium Platinichloride.*—Marks very visible. Continued to slowly deepen, and in a few weeks were almost black.

*Silver Carbonate.*—The traces of the rod were brown. When the paper was placed in ammonia the carbonate dissolved, but the marks resisted the action of the ammonia and remained.

*Silver Phosphate.* — Action very similar to the preceding.

*Silver Arsenate.*—Similar action.

*Silver Tartrate and Oxalate.*—These salts gave analogous results to the preceding, but not so well marked. The carbonate phosphate and arsenate show this reaction best and about equally well. What is rather curious is that silver chloride does not exhibit a visible action.

*Mercuric Oxide.*—Paper imbued with a saturated solution of mercuric nitrate and then treated with solution of potash and dried shows this reaction very distinctly. Mercuric oxide appears to be quite sensitive to light.

*Turpeth Mineral.*—Mercuric sulphate was dissolved in water with the aid of sulphuric acid. Paper was soaked in the solution, allowed to become nearly dry and then washed. This paper showed the reaction very moderately, but the marks were brought out more strongly by immersion in ammonia.

*Ferric Alum (Ammonia).*—Paper imbued with solution of this salt dried and marked was immersed in solution of potassium ferridcyanide. The marks came out blue, showing that the ferric salt had undergone partial reduction.

It is easily conceivable that the action of shearing stress should be enormously greater than that of simple pressure. For it seems probable that pressure can only cause decomposition when the resulting product is more dense, has a greater specific mass, than the original substance. With shearing stress the case is altogether different. All matter is in a state of vibration, and it is easily conceivable that the forcible friction of a hard substance may increase vibration in somewhat the same way as does a bow drawn over a stretched cord. Both the elasticity and the tension of the atoms themselves are vastly greater than those of any stretched cord, so that the increased vibration may easily be sufficient to shatter the molecule.

The transformation of light, heat, and electricity into mechanical energy as well as the converse transformations are extremely familiar. That mechanical energy may be transformed into chemical energy is proved by the results in these papers described. The converse transformation, that of chemism into work, is in an industrial point of view by far the greatest chemical problem now waiting for solution. But it is by no means certain that such a transformation is practically possible. At least it seems probable that the improvement in our method of obtaining work from the chemism of carbon may be in the direction of substituting electricity for heat as the intermediary.

## LONDON WATER SUPPLY.

### Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending November 30th, 1893.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To Major-General A. De Courcy Scott, R.E.,
*Water Examiner, Metropolis Water Act, 1871.*

London, December 12th, 1893.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined two were recorded as "clear, but dull," the remainder being clear, bright, and well filtered.

Comparing the average composition of the five Thames-supplied waters during the month of November with that of the corresponding month last year, we see considerable differences. In November, 1893, the common salt, nitric acid, and hardness are practically the same as they were last year, but in the other constituents—those which may be termed the contaminating factors—the month just ended shows a diminution of more than 50 per cent, whilst the brown colour, a good rough criterion of the organic matter present, has sunk from 24·5 to 15·5. This improvement is well seen by reference to the following Table :—

*Comparison of the Averages of the Five Thames Supplies for the Months of November*, 1892 *and* 1893.

| | Common salt per gallon. | Nitric acid per gallon. | Hardness, degrees. | Oxygen required per gallon. | Organic carbon per gallon. | Organic carbon per gallon. | Colour. Brown. Blue. |
|---|---|---|---|---|---|---|---|
| | Means. | Means. | Means. | Means. | Means. | Maxima. | Means. |
| 1892 | 2·238 | 0·839 | 16·29 | 0·076 | 0·142 | 0·199 | 24·5 : 20 |
| 1893 | 2·248 | 0·766 | 15·33 | 0·033 | 0·068 | 0·096 | 15·5 : 20 |

As compared with the composition of the October waters, that of November shows scarcely an appreciable difference, and for all practical purposes they may be looked upon as of the same excellent quality that has characterised the waters for several months past.

Again we have to record a deficient rainfall. Whilst the mean rainfall for twenty-five years at Oxford has been 2·31 inches for the month of November, there has actually fallen 1·68 inches during the month, giving a deficiency of 0·63 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.

## ON ALGINE.

By A. M. VILLON.

Algine is a mucilaginous matter resembling gum arabic, obtained by Mr. Stanford from the red algæ or laminariæ (*L. stenophylla* and *L. digitata*).

It is manufactured in the following manner :—The seaweeds are treated with a boiling solution of sodium carbonate, which dissolves the alginic acid in the form of sodium alginate, and leaves as a residue the cellular tissue of the plant, consisting of a special cellulose named algulose. The alkaline solution is filtered and treated with hydrochloric acid, which precipitates the alginic acid in a gelatinous state, of an amber colour. The precipitate is separated by means of the filter-press, re-dissolved in a solution of sodium carbonate, evaporated to a thick consistence, and finally dried by being spread in flat vessels of porcelain or glass placed in a stove moderately heated, as is done with albumen.

*Soluble algine*, which is an alkaline alginate, appears in the form of flexible transparent laminæ of the following composition :—

| | Per cent. |
|---|---|
| Water .. .. .. .. .. .. | 18·22 |
| Organic matter .. .. .. | 59·05 |
| Sodium carbonate . .. .. | 18·05 |
| Neutral salts . .. .. .. | 2·87 |
| Insoluble substances .. .. | 1·81 |

Algine is very similar to gelatin, but it differs by not coagulating to a jelly, and by not being precipitated by tannin. If differs from albumen by not being coagulated by heat. It differs from gum arabic because it is precipitated from its solutions in an insoluble state by the mineral acids and by the oxalic, tartaric, citric, lactic, and picric acids.

Algine forms soluble salts with the alkalis. By double decomposition with the metallic salts it yields alginates which are insoluble, except those of magnesium and manganese.

The solutions of algine are very viscid. It has fourteen times the viscidity of starch, and thirty-seven times that of arabic. This property enables it to be used in tissue-printing as a thickener, in place of gum or dextrin.

It gives cloths a thick, soft, elastic handle, and furnishes a transparent dressing, which may be made insoluble and impermeable by taking the cloth through a dilute solution of algine and then through very dilute hydrochloric acid, which fixes the alginic acid on the fibres in an insoluble state.

The alkaline alginates may be used as salts for "dunging," for fixing iron and aluminium mordants upon cotton tissues.

Aluminium alginate, dissolved in ammoniacal water, serves to render cloth waterproof. It is merely necessary to steep the cloth, and to aërate it so as to expel the ammonia, when the aluminium alginate is left in the pores of the cloth in an insoluble state. In this manner we have rendered leather impermeable.

Aluminium alginate is used as a mordant.

Copper alginate dissolved in ammonia-water has been proposed for impregnating substances to preserve them from decomposition or from the attacks of insects. We have employed it successfully against the cryptogamic diseases of the visa. The double iron and ammonium alginate is employed in medicine as a styptic.

A mixture of sodium dichromate and alginate is sensitive to light.

Algine has been proposed as an anti-incrustation agent in steam-boilers, as it precipitates calcareous salts.

Lastly, it is employed for emulsifying oils and clarifying wines and spirits.

Insoluble algine is alginic acid.—*Société Chimique de Paris.*

## ON METALLIC SEPARATIONS IN ALKALINE SOLUTION OF HYDROGEN PEROXIDE.

By PAUL JANNASCH.

*Behaviour of Copper Solutions.*—If to the neutral solution of a copper salt there is added dilute ammonia, drop by drop, until the precipitate first formed is just re-dissolved, and if we then add a 3 per cent solution of hydrogen peroxide, the liquid froths up briskly, and we obtain a bulky flocculent precipitate of black olive-greenish percupric hydroxide. Unfortunately I have not yet succeeded in effecting this precipitation quantitatively, for in numerous trials with about 0·5 grm. of copper sulphate, in different concentrations and at different temperatures, appreciable quantities of copper (averaging 1·5 to 2 per cent copper oxide) remained in solution. For these approximately quantitative precipitations large quantities of hydrogen peroxide were required (150 to 250 c.c.). Further, on weighing the results were invariably too high, in consequence of the presence of considerable admixtures of silica, which showed that hydrated copper peroxide in an alkaline liquid somewhat attacks the porcelain vessels.

On studying the influence the presence of organic substances, such as tartaric acid, exerts upon the precipitation of copper by hydrogen peroxide, I had the opportunity of observing a remarkable chemical action, by means of which we can, on the one hand, demonstrate the simultaneously oxidising and reducing properties of a compound which easily gives off oxygen, and, on the other hand, the formation of all three stages of oxidation of copper in one and the same reaction. For this purpose we precipitate a solution of copper sulphate in a roomy test-tube with an excess of soda-lye (copper hydroxide); add then so much tartaric acid as to produce a clear solution of hydrogen peroxide until there appears an abundant precipitate (hydrated copper peroxide). If this precipitate is then rapidly heated over a high flame the precipitate entirely disappears with brisk effervescence, whilst the liquid takes transitorily a splendid dark velvetty green colour, and, when it has again become blue, there is lastly formed an abundant yellowish-red deposit of cuprous oxide. The separation of cuprous oxide generally ensues suddenly, when the liquid is removed from the flame and allowed to remain for a short time undisturbed. Thus the entire process is a so-called "time-reaction." The author used—

1. A mixture of 2 c.c. solution of copper, 3 c.c. tartaric acid, 4 c.c. soda-lye, and 15 c.c. hydrogen peroxide at 2 per cent gives, after a momentary effervescence, on cooling, an abundant deposit of bright red granular cuprous oxide.
2. Two c.c. copper sulphate, 1 c.c. tartaric acid, 1 c.c. soda-lye, and 10 c.c. hydrogen peroxide give, after boiling until the restoration of the blue colour, a reddish-brown flocculent deposit, whilst the liquid is decolourised.
3. Two c.c. copper sulphate, 1 c.c. tartaric acid, 0·5 c.c. soda-lye, and 5 to 10 c.c. hydrogen peroxide yield a flocculent pale green deposit, which on prolonged standing becomes a heavy yellow sediment, with fine light blue supernatant flakes.
4. Two c.c. copper sulphate, 1 c.c. tartaric acid, 0·5 c.c. soda-lye, and 15 c.c. hydrogen peroxide give a light blue precipitate unchanged on boiling.—*Ber. der Deutsch. Chem. Gesell.*

## ON LIFE AT LOW TEMPERATURES.

By RAOUL PICTET.

In the 76th meeting of the Swiss Society of Naturalists, held at Lausanne, from the 5th to the 8th of September, the author described the struggle of Nature against external attacks. If a dog is placed in a copper receiver, cooled down to −60° to −90°, its temperature rises by half a degree in the first ten minutes. On prolonging the experiment the extremities become cold, but the body resists for some time. After 90 minutes the temperature falls by 1°. Then follows a point where the struggle is given up, the temperature falls rapidly, and the animal dies suddenly. Pictet has made similar experiments on himself and others, exposing his arm to such low temperatures. Pain occurs within the arm on the periosteum, whilst the epidermis experiences no pain.

All insects resist a cold of −28°, but not of −35°. Myriapods resist down to −50°, and snails to −120°. The eggs of birds lose their vitality at −2° or 3°, the eggs of ants at 0°. Frog-spawn bears −60°, and silk-worms' eggs −40°. Infusoria died at −90°, and bacteria retained their virulence at −213°. This cold was produced by frozen atmospheric air.—*Chemiker Zeitung.*

## ANALYSIS OF THE BUTTERS OF COMMERCE.

By C. VIOLETTE.

The method which I employ comprises two series of operations; in the former the butters are classified according to their specific gravities taken at 100°, in three groups—the margarinised butters, the doubtful butters, and the pure butters and those which may be considered as such.

*Classification of Butters.*—When operating by the bottle method upon pure butters, margarines, and mixtures, and taking account of all the necessary corrections, I have found—1, that the weight in a vacuum of 1 c.c. of butter, at 100° varies in general from 0·86320 grm. to 0·86425 grm.; 2, that for margarines this same quantity varies from 0·85766 grm. to 0·85865 grm.; 3, that the density of a mixture of butter and margarine is exactly the mean of the density of the constituents; 4, that beasts principally fed on hay yield butters the densities of which are close upon 0·86320, whilst cattle chiefly fed on grass, pulps, cakes, and farina yield butters of higher densities, close upon 0·86425; 5, that in more than 150 samples examined I have found only two obtained from cattle of Le Nord, and well nourished with oil-cakes, &c., which had densities reaching to 0·86530 and 0·6540; and a single one, from a cow fed on straw and dry hay, had a density of 0·86277. These three exceptions, from a general point of view, have little importance.

The exact determination of the densities of a certain number of samples of butter, of margarine, and of mixture, have furnished me with bases for the graduation of a densimeter which shows at 100° all the densities comprised between those of margarine and of butter. This instrument is extremely sensitive, for the units of the fourth decimal place occupy on the scale a length of 1·4 millimetre. A simple reading on the stem of the instrument plunged into butter heated to 100° enables us to establish the classification of a butter in one of the three categories above mentioned.

The apparatus which enables me to heat fatty bodies conveniently and rapidly to 100° is composed of a water-boiler formed of two cylindrical parts connected by a small bent-piece. The steam-chamber of the boiler communicates with a worm cooled by a stream of water. On the platform, situate below the first joint, is soldered a test jar of tinned copper, fitted at its lower part with a tube having a cock opening outwards, and permitting the fatty substance to be withdrawn after each operation. The boiler is set vertically upon a covering support, and heated by means of a strong gas-burner. A quarter of an hour is sufficient to raise the fatty substance to 100°, indicated by a thermometer. The melted butter is stirred repeatedly, raising and lowering the densimeter, and the degree is noted after allowing it to rest for a few moments.

This arrangement, necessary for my researches, which extended at once to butters, margarines, and their mixtures, has the inconvenience of requiring a considerable quantity of the sample, about 480 grms. of melted butter. To obviate this inconvenience I have subdivided the densimeter into a series of smaller floaters, graduated by comparison with the type instrument. Their volume is 36 c.c., and they require only 50 grms. of butter for each observation.

A simple floater, No. 1, enables us at once to classify the butters. The stem has merely three marks; that in the middle corresponds to the density 0·86266; the lower one, 0·86320, for very numerous pure butters; and the upper mark corresponds to the density 0·86215, which indicates a proportion of 25 per cent of margarine in a medium butter. If the level of immersion is between the middle and the lower lines, it may happen that the butter is pure, but it is very probably mixed with margarine. This is why I regard such butters as doubtful, and put them aside for a more complete examination by chemical methods. If the floating-level is at the lower mark and below, it will be well to make use of the floaters No. 2 and No. 3, the marks on which, corresponding to higher densities, permit us to ascertain the nature of the butter. In case the floating-level is above the higher mark, we have recourse to another series of floaters comprising the densities of 0·86266 to 0·857, and indicating the approximate proportions of margarine.

This classification cannot be absolute, since butters of high density may be brought to a marginal density by the addition of margarine. Thus the expert should be careful to work, from time to time, upon the mean butters of the region, so as to know their normal density. In general this density varies little for butters obtained from cattle fed on the same diet. Thus butters obtained from cattle feeding in Calvados, Côtes-du-Nord, Tarn, Ardennes, and Loire (May, 1891), had densities between 0·86415 and 0·86465, the range being 0·0005. A butter from the dairy of Braine-le-Comte (Belgium, Nov., 1892), derived from the milk of thirty-three farms, had the density 0·86425. The butter of a single cow of this dairy had the density 0·86385: difference, 0·0004 grm.

The application of this method does not require special chemical knowledge. It is rapid in execution, permitting an operator with an assistant to classify easily a hundred samples per day. The doubtful butters are reserved for a chemical examination the particulars of which I will shortly describe.—*Comptes Rendus*, cxvii., p. 856.

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## RESEARCHES ON SAMARIUM.

By LECOQ DE BOISBAUDRAN.

I have elsewhere said that the reversal bands of Sm change their relative lustre with the experimental conditions. Thus $Z\zeta$ 614·4 gains a little as regards the orange when the spark is very short, when the solutions are concentrated, when there is a great excess of HCl, a case in which $Z\zeta$ even slightly passes the orange (with the spark in the middle of the liquid), &c. These observations have led me to suppose that the increase of $Z\zeta$ at the head of the fractionation by $NH_3$ was perhaps due to changes in the experimental conditions. I have therefore anew compared the head and the middle of this fractionation, endeavouring to equalise the conditions.

The increase of all the fluorescence and the relative increase of $Z\zeta$ seemed then decidedly less pronounced, though they were still observed in passing from the middle to the head of the fractionation by $NH_3$. The electric rays, $Z\epsilon$, were also found a little more marked at the head than at the middle, the difference, however, being less than that previously observed.

I have fractionated very carefully, by $NH_3$, the head of my previous fractionation by oxalic acid, which had itself been effected on the head of the first fractionation by $NH_3$. The very small mass of matter left in the oxalic tailings contained all the $Z\beta$. If the relative strengthening of the $Z\zeta$ observed at the head of the first fractionation by $NH_3$ was due to the concentration of any particular element, we might expect that this intensification would be much heightened at the head of the second fractionation by $NH_3$, which is, moreover, the last practicable, on account of the extreme scantiness of the matter.

In the head of the last fractionation by $NH_3$, $Z\zeta$ has not a relative lustre greater than in the tailings, where the other bands are slightly brighter than at the head, and where we do not see a trace of $Z\beta$, no more than at the head. But both at the head and at the tailings of the last fractionation $Z\zeta$ is relatively and absolutely slightly superior to what it is at the middle of the first fractionation by $NH_3$.

Besides the reversal bands of samarium already described—red, orange-red, orange (double), and green—there exists another green band, much weaker, which I have observed long ago, and which is not without interest. Its maximum of luminosity (measured on the prismatic scale) is $\lambda = 535{\cdot}4$ (a mean of the best measurements). The band is very cloudy, especially to the left, and it is distinctly narrower than the first green (maximum of the first green $\lambda = 560{\cdot}6$). The brightness, always very moderate, varies with the experimental conditions, the nature of the acid, and also slightly with the portion of the fractionation.

The band 535·4 seems to gain a little when the spark strikes at the margin of the liquid instead of being drawn near the centre, and when the spark is very short. It is seen better in a very acid hydrochloric liquid than in a solution which is nearly neutral. It is a little stronger in $NHO_3$ than in HCl. It is also produced in an acetic solution, although rather more feeble than in HCl. The band 535·4 is slightly stronger at the head than at the middle of the fractionation by $NH_3$.

*Comparison of $Z\zeta$ and of* 535·4.—Nitric acid strengthens these two bands with respect to the orange, but the increase of $Z\zeta$ is by far the greater. The two bands are so much better developed in the hydrochloric solution the more acid it is (always provided that the quantity of HCl is not such as to precipitate $Sm_2Cl_6$). The two bands were slightly more marked at the head than at the middle of the first fractionation by $NH_3$. They gain a little with the shortness of the spark. The band 535·4 is only slightly enfeebled by acetic acid, whilst $Z\zeta$ is extinguished or reduced to a trace. $Z\zeta$ gains very distinctly if the spark strikes at the middle of the liquid, but 535·4 seems rather to be enfeebled.

I have already mentioned the extinction of $Z\zeta$ by acetic acid (said to be pure). I believe, however, that I have seen $Z\zeta$ faintly with a concentrated acetic solution. The red and green bands (643·4 and 560·6) seemed a little more developed (with reference to the orange) than in solution in HCl. The addition of a volume of acetic acid (at 8°) weakened 535·4 slightly and rendered $Z\zeta$ very feeble or null, but rather strengthened the other bands.

With $NHO_3$ the red and green bands (643·4 and 560·6) are distinctly stronger with reference to the orange than with HCl, but this increase is less than that of $Z\zeta$.

I had previously measured the ray rather cloudy but narrow which forms the right margin of $Z\zeta$, and found $\lambda = 611{\cdot}2$. Having repeated this measurement, I again found $\lambda = 611{\cdot}2$.—*Comptes Rendus*, cxvii., p. 199.

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## ON THE
## PREPARATION OF METALLIC LITHIUM.

By M. GUNTZ.

The preparation of metallic lithium might seem at first sight an easy operation, but on repeating the experiments of Bunsen, Hillier, and Troost we quickly perceive, on making quantitative determinations, that the yield, though very variable in different operations, is in general extremely low with reference to the intensity of the current employed.

On studying the best conditions for the preparation of lithium, we have found that the yield of metal is so much the higher as the temperature of the electrolysis is lower. An impure salt, containing potassium and sodium chlorides, gives, when electrolysed at its melting-point, much better results than pure lithium chloride. This result led us to lower the melting-point of the lithium chloride by the addition of potassium chloride. I have found that LiCl melting about 600°, the mixture of LiCl and KCl at equal weights melts about 450°. A mixture of equal mols. of the two chlorides melts about 380°; a mixture of 2 mols. KCl with 1 mol. of LiCl melts at 550°; and pure potassium chloride melts at 740°. The most favourable mixture for electrolysis contains equal weights of the two chlorides. This mixture can be easily kept in fusion below 450°; and, moreover, during the electrolysis the mixture loses lithium chloride and its fusibility becomes greater. This is not the case with the mixture formed of equal mols. of LiCl and KCl, the fusibility of which diminishes rapidly under the same conditions.

To obtain large quantities of lithium we heat from 200 to 300 grms. of the mixture of the two chlorides in equal weights in a porcelain capsule over a simple Bunsen burner. The mixture melts very readily, and the two electrodes are then introduced. The positive electrode is a rod of carbon of about 8 m.m. in diameter; the negative electrode is a rod of iron from 3 to 4 m.m. in diameter, which is placed in the axis of a glass tube of 20 m.m. in diameter. The current is passed in, and the experiment goes on very rapidly by using, *e.g.*, an electromotive force of 20 volts and a current of 10 ampères. At the end of an hour the lithium exceeds the level of the liquid in the glass tube by more than a centimetre. To extract the metal the tube is raised after interrupting the current; the lithium floats on the surface of the melted chloride without igniting. It is taken up in an iron spoon and poured into a dry ingot mould.

The metal thus obtained is free from iron and silicon, but contains 1 per cent of potassium by weight, which corresponds to 1 atom Ko to 273 atoms Li. For most uses the metal is sufficiently pure.

When the electrolysis is effected at a red heat, about 700°, with pure lithium chloride, the metal arriving at the negative pole combines with the chloride to yield a lithium sub-chloride, $Li_2Cl$, which remains at the negative pole. This compound, less conductive than the original chloride, diminishes the intensity of the current as it is observed at the ammeter. This sub-chloride, being diffused in the melted liquid, arrives at the positive pole, where it recombines with the chlorine with emission of light; this compound producing oscillations of the needle of the ammeter. When the temperature of electrolysis reaches 500° or even falls lower, the lithium does not combine with lithium chloride, and is found altogether at the negative pole, and may be collected. This is the reason of the high yield obtained in this case.

This phenomenon of the formation of metallic sub-chlorides by electrolysis seems general for the alkaline metals. I have not yet been able to obtain by this method compounds in a state of satisfactory purity.—*Comptes Rendus.*

## THE STABILITY OF STANDARD SOLUTIONS OF TARTAR EMETIC.*

By HIPPOLYTE GRUENER.

During the progress of some investigations on antimony, I found it desirable to know to what extent a solution of tartar emetic could be relied on to retain its strength when kept for a length of time. Accordingly I made up a number of solutions of tartar emetic, whose strength was determined by titration in presence of an alkaline tartrate and bicarbonate with decinormal iodine, standardised against arsenious oxide. These solutions were put aside in stoppered bottles for a number of months, when they were again determined with iodine standardised against the same arsenious oxide.

Solution A was simply tartar emetic in distilled water, 16 grms. to the litre. At the end of five months this was found to have lost strength to a considerable extent, while a deposit, seemingly a mixture of antimonious oxide and of fungus growth, had settled at the bottom of the bottle. At the end of fourteen months a still greater loss of strength was observed, corresponding in all to about 3·5 per cent. of the tartar emetic, of which 4 grms. were present. The sediment was drained, dissolved in tartaric acid, and titrated with iodine. It was found to correspond to 0·13 grm. of tartar emetic or approximately the amount lost. This shows clearly that under the conditions no great loss is caused by the formation of the pentoxide, in closed bottles at least.

Solution B was slightly alkaline with sodium bicarbonate in presence of sodium tartrate. On this solution after five months there was developed in addition to a fungus growth a deposit, probably antimonious oxide; there was here a slight loss in the strength of the solution, amounting to 1 per cent.

Solution C was acid with tartaric acid only. After ten months the solution was found of the same strength and clearness as it was originally; but four months later there was a slight deposit accompanied by a loss of 1·2 per cent.

Parallel experiments to A gave like results. Two repetitions of C with varying amounts of tartaric acid present showed in each case a decided fungus growth with no loss of strength at the end of five months, whereas at the end of nine months the loss amounted to 1 per cent. for the larger amount of tartaric acid and 0·3 per cent for the smaller amount.

It seems then that there is little danger of any oxidation of the antimonious oxide occurring, and provided enough tartaric acid is present to keep all the antimonious oxide in solution, the solution should maintain its strength for at least five or six months. The fungus growth has not been found to interfere in practical work with the solutions, yet it seemed advisable to prevent its formation if it could be done simply. To test the possibility of this, a number of solutions were prepared containing varying amounts of hydrochloric acid, which should act as a steriliser; enough tartaric acid was added to counteract any tendency towards precipitation. In one series of experiments the solutions were sterilised at the beginning by boiling; in the other series distilled water which had been exposed more or less to the air for a number of days was directly used. Where the solutions had been thus sterilised no sign of fungus growth had appeared at the end of five months, and in the case of the unsterilised solutions there was never more than a trace. Where the hydrochloric acid present was not more than 10 c.m.$^3$ to 500 c.m.$^3$ of water, there was at the end of three months only the faintest trace of a deposit and no material loss of strength. Where the hydrochloric acid was present to to the extent of 25 c.m.$^3$ in 500 c.m.$^3$ of water a decided granular precipitate was observed, accompanied by a loss of strength of about 10 per cent. The granular precipitate dissolved in tartaric acid and titrated accounted almost exactly for this loss.

A number of solutions were prepared under varying conditions and left open to the air for three months, at the end of which time no loss from oxidation was found.

It may be seen that tartar emetic in a solution of 16 grms. to the litre is not oxidised either in closed or open bottles. If it is desired to keep this solution as a standard for a moderate length of time it can be done in presence of enough tartaric acid (20 to 30 grms. to the litre) to prevent precipitation. The addition of 1 c.m. hydrochloric acid to one litre of solution is enough to prevent any decided formation of fungus growth, at the same time not enough to cause a deposit, as happens when large amounts of hydrochloric acid are used.

In the titration of tartar emetic in presence of starch the permanent blue colour was taken in every case as the indication of the end reaction, as all other shades of colour were found unsatisfactory. It is a well known fact that in the titration of antimony salts the colour of the starch iodide is not developed until there is a considerable excess of iodine present, so that as compared with arsenious oxide, iodine gives high results with antimony. Thus, for example, the mean of six series of determinations made at various times and aggregating twenty-nine determinations showed the presence of 43·95 per cent of antimonious oxide in tartar emetic. (Sb = 120 and tartar emetic $KSbOC_4H_4O_6.\frac{1}{2}H_2O.=332$, requiring 43·37 per cent).

The facts above shown, that tartar emetic may be kept in stable solution by means of tartaric acid and hydrochloric acid in the proportions given, make it possible to use and keep such solutions for standardising iodine for the determination of antimony, and thus to eliminate the error due to the tardy development of the starch iodide blue in presence of antimony salts, observed when compared arsenious oxide is used as a standard.

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* From the *American Journal o Science*, vol. xlvi., Sept., 1893.

On the Acyclic Isomers of Borneol.—Ph. Barbier.—These compounds are coriandrol and licareol. Licareol possesses a double isomerism, optical and geometrical, and exists in four distinct modifications: 1. Instable sinistro-licareol from the essence of licari, the stable isomer of which is dextro-licarhodol. 2. Instable dextro-licareol from essence of coriander, the stable isomer of which is sinistro-licarhodol.—*Bull. de la Soc. Chim. de Paris*, ix. and x., No. 23.

## NOTICES OF BOOKS.

*Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes:* Their Proportions and Properties, and the Manufacture therefrom of Candles, Soap, and other Products. By C. R. Alder Wright, D.Sc. (Lond.), B.Sc. (Vict.), F.R.S. With 144 Illustrations. London: C. Griffin and Co.. Limited. 1894. 8vo., pp. 570.

It must be admitted that, of all the groups of natural organic substances, the fatty oils admit of the most numerous and varied uses, and that, at the same time, they are open not merely to natural fluctuation in their qualities, but to elaborate sophistications. Hitherto we have had, in the English language on these subjects, papers read before our learned Societies and inserted in the scientific and technical press, but no complete monograph treating of the oils and fats more comprehensively and in fuller detail than it is possible to do in general works. Dr. C. R. Alder Wright has supplied this deficiency in a manner which we may safely pronounce admirable. He has not merely "read up" the mass of information to be found in existing authorities, English and foreign; he has verified and digested their statements. He does not enter upon an examination of the mineral and volatile oils. From considerations of space he disclaims the attempt at a minute discussion of the analytical methods required in each possible case of sophistication.

Assuming general chemical principles as known to the reader, he commences with a general view of the composition of the oils, fats, &c., and their sources. He then enters upon saponification in the widest sense of the term, and of its products, alcoholiform and acid.

The section on physical properties of oils brings us to their characters as assisting in the recognition of their nature. We have here reference to the cohesion figures of Tomlinson, to the taste, odour, and colour of oils, their behaviour with polarised light, their solubility in various solvents, their fusing and solidifying points, specific gravity, their relative densities as affected by temperature, and on viscosimetry.

The next section enters upon the chemical properties of the oils, the separation of their constituents, the determination of the free-acid number, of unsaponifiable constituents, of water, and of suspended matters—too commonly present in lard and tallow.

A succeeding chapter treats of flashing points—important, of course, chiefly in mixtures containing mineral oils,—of the elaidin reaction, the nitric acid test, and the zinc test.

Among the quantitative reactions figure the Kœttstorfer test, the saponification equivalents, Hehner's test, Reichert's test, the bromine process, the iodine process, Hübl's test, and the tests of Benedikt and Ulzer, and of Zeisel.

The fourth section describes the processes used for extracting, rendering, refining, and bleaching oils, and the recovery of fatty matters from soap-suds.

In Section V. we find the classification of oils into the olive, the rape, the castor, the lard oils, the cotton-seed, the linseed and the train classes, the vegetable butters and waxes, the animal butters, the sperm oils, the non-glyceric waxes, and the bees'-wax class. Hereupon follow the principal uses of oils and fats,—*e.g.*, margarine, lamp oils, oils for paint and varnish, lubricants, Turkey red or alizarin oils, and lanoline.

The detection of adulterations is particularly given for the cases of olive oil, rape and colza, linseed, sperm, tallow, bees'-wax, and spermaceti.

The question whether the wax of bees, &c., is a secretion due to their own vital action, or is a substance precontained in the pollen and nectar of the flowers, is not absolutely decided, though the author gives reasons for accepting the former view. It is stated, in a note, that wax from the Bordeaux district is the most difficult to bleach.

The remainder of the book is devoted to the great industries of candles, soap, and glycerin. Notwithstanding the rise and progress of gas and of paraffin oils, the candle manufacture is far from declining. Simplicity and portability give the candle an advantage which in many cases outweighs its higher cost. As regards toilet soap, the author has in his "Cantor" lectures proposed their classification into three grades, according to the amount of free alkali present. This objectionable constituent may range from 0·2 to 7·5 per cent. He points out that sugar, very generally present in transparent soaps, is as irritating to the skin as free alkali, and that some of the essential oils used as scents are open to a similar objection.

We do not find any mention of the "soap-powders" and "extracts of soap" so extensively advertised, and employed by manufacturers and laundresses.

The only flaw we can find in this excellent work is that the author terms cocoa-nut oil "coker-nut" oil. This is, we believe, the first time that this vulgarism has found its way into scientific literature. To prevent the confusion between the cocoa-nut, the chocolate-nut, and the cuca, it would be surely better to call the first-mentioned product cocos-nut.

As a whole, Dr. Alder Wright's work merits to be accepted by all dealers in and manufacturers of the oily and fatty products as *the* standard authority.

*Intensity Coils; How Made and How Used.* By "Dyer." With a Description of the Electric Light, Electric Bells, Electric Motors, the Telephone, the Microphone, and the Phonograph. Eighteenth Editon. London: Perkin, Son, and Rayment. 8vo., pp. 79.

We have had the pleasure of noticing a former edition of this little work, and we feel by no means inclined to retract what we then said.

Several additions have been made, which will distinctly increase the value of the present book. The most interesting is entitled "Seeing by Electricity," and refers to an invention which if realised must throw all the "phones" completely into the shade. Imagine switching on a wire and being able to see in a camera lucida what is going on in a different room.

*Catalogue of Chemical Apparatus, Balances, Drying Ovens, Furnaces, Laboratory Stands, &c.* Part III. London: Gallenkamp and Co.

This part contains chiefly appliances of metal, wood, &c. Balances figure here very largely, of the makes of Sartorius, Becker and Sons, Roberzahl, and Rueprecht. All the sets of weights—metric of course—are made on the principle, objectionable as it seems to us, of the rejection of all weights which are not sub-multiples of 10. We will venture to say that the metric system would be more frequently adopted in England but for its nomenclature and its arrangement of 5, 2, 1, 1.

In appliances for the production and application of heat, whether by means of oil, gas, coke, charcoal, &c., the Catalogue is very rich. The furnaces of Fletcher, Luhme, Sefström, Hempel, Griffin, L. Meyer, Erlenmeyer, &c., are figured and described.

Incubators, sterilisers, and thermostats are shown of different makes, together with the additional apparatus used in bacteriological research.

In a letter Messrs. Gallenkamp tell us that the lower scale of prices is for the convenience of consumers who order their requisites direct from the manufacturers in Germany. The higher figures charged at their London establishment are to cover the risk of transit.

The firm also state that the reason why the earlier parts of the Catalogue were printed in Antwerp is cheapness. They tell us that the lowest estimate they could obtain in England was £100 for 2000 copies, whilst the Antwerp printers offer 3000 copies for £50. This is certainly a substantial difference, but we hope that Messrs. Gallenkamp will not come in collision with Trades-Unionism, which is now the ruling power in England.

*Micro-Organisms and Fermentation.* By Alfred Jörgensen, Director of the Laboratory for the Physiology and Technology of Fermentation at Copenhagen. New Edition. Translated from the re-written and much-enlarged Third Edition in German, by Alex. K. Miller, Ph.D., F.I.C., and E. A. Lennholm, and revised by the Author. With 56 Illustrations. London: F. W. Lyon. 1893.

This work, says the author, appeals to chemists, botanists, and biologists,* likewise to those technologists who are engaged in the branches of industry named.

Herr Jörgensen's work is specially devoted to a study of the microbia of alcoholic fermentation, and takes merely an incidental notice of the septic and pathogenic organisms. Hence it is to be hoped that the watchful dragons of bestiarianism will not roar for its "withdrawal."

The first chapter of this work treats of staining, sterilisation, disinfection, nutritive media, the preparation of pure cultures, and the enumeration of yeast-cells. Under "Disinfection" we find the interesting remark that disinfectants, when very much diluted, may act upon the yeasts as *stimulants*. Alcoholic fermentation is promoted by the addition of mercuric chloride in a dilution of 1 : 300,000, by solution of salicylic acid at 1 : 6000, or boracic acid of 1 : 8000. This is very suggestive.

Pure cultures for morphological research seem to have been first employed in 1821 by Ehrenberg. Of the production of pure cultures for physiological inquiries, the first method, that of dilution, seems to have been originated by Lister in 1878, and was further developed by Hansen in 1881. Schröter, in 1872, first employed solid nutrient media, *e.g.*, slices of potato. The improved method of plate culture was due to Koch, in 1883. For yeasts Hansen's modification is a further advance, though for bacteria the plate-method is still the best at our disposal.

The second chapter takes up the examination of air and water. We learn that the atmospheric microbia are very apt to occur in groups or clouds, whilst the intervening spaces are either germ-free or contain merely isolated micro-organisms.

Chapter III., which treats of bacteria, opens with the unquestionable statement that the more our knowledge of these micro-organisms becomes enlarged the more difficult it becomes to give a general definition of them. It is found that one and the same species of bacterium can occur in very different forms. Hence our names for these organisms often express merely growth-forms of the same species, and not distinct species. We have then to encounter the question—"Under what conditions does a species occur in this or that particular form?"

In this connection we find mention of Pasteur's important discovery of the two classes of microbia, the anaërobic and the aërobic, between which Duclaux recognises intermediate forms.

Among the forms which chiefly concern the fermentation industries we find mention of the butyric bacteria, the spores of which can resist the temperature of ebullition for three to twenty minutes; but they are killed on exposure to 90° for six hours in a solution of glucose, and in glycerin for six to eleven hours.

The growth of moulds is considered a sign that other growths of a more injurious character are also present.

Our present knowledge of the alcoholic ferments, an ill-defined class, is mainly owing to the researches of Hansen. The researches of this *savant* are fully recognised both by practical brewers and by scientific men. The opinion is expressed that, thanks to Hansen's method, the pure yeast question has been solved both for top fermentation and bottom-fermentation.

The work concludes with an elaborate bibliography of the literature of fermentation. To all persons engaged in the manufacture and commerce of alcoholic liquids this work must prove a treasure.

*Agricultural Journal:* Published by the Department of Agriculture of the Cape Colony. Vol. vi., No. 22.

*Maize and Wheat Exhibits at Chicago.*—In a paper by Edmund Mitchell bearing this title we find the strange statement that, "except in Southern Europe, maize cannot be matured in the Old World." We think some of the readers of the *Agricultural Journal* will be startled at learning that "mealies" will not grow in Africa!

*Boring for Water.*—Artesian wells seem to have been successfully carried out at Albert and Colesberg. At Hanover, Hope Town, and Jansenville, flowing water was less generally obtained, though enormous supplies rose to within a short distance of the surface. It is pointed out as a delusion to expect that an abundant flow may always be found on going deep enough.

There is good prospect of a great improvement in the quality of Cape wines by the introduction of pure selected ferments.

The avidity of the potato for potash is distinctly pointed out. On the other hand, soda is a poison to the plant. Are there no potash deposits or potassiferous waters in South Africa?

*Practical Agricultural Chemistry for Elementary Students.* By J. B. Coleman, A.R.C.Sc., F.I.C., and F. T. Addyman, B.Sc., F.I.C. London and New York: Longmans. 1893. Small 8vo., pp. 88.

The work before us is a treatise on qualitative analysis, arranged with especial reference to the wants of agricultural students. The first section treats of chemical apparatus and manipulations.

A second section is devoted to the constituents of air and water. In the third section we have experiments on soils, manures, feeding materials, and dairy produce. Section four embraces instructions for the recognition of the metals and the acid radicles, with tables for qualitative analysis. The fifth and concluding section includes instructions concerning apparatus, chemicals, and reagents with various useful tables.

The instructions given are sound and accurate, and are clearly described. Another good feature of the book is that it contains no reference to any "syllabus" or examination. The experiments described can be performed at a very small outlay for apparatus and reagents. Hence the work is well suited for schools in which economy is a necessary consideration.

*Select Tables from the U.S. Pharmacopœia* (1890). Reprinted for ready reference in daily practice. Published by the Committee of Revision, 1893. Philadelphia: J. B. Lippincott Company.

These tables comprise an alphabetical list of volumetric assays, *i.e.*, of standard solutions for volumetric analyses, with the accompanying indicators, also E. R. Squibb's alcoholometric table, the saturation tables of the U.S.

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* The term biology and its paronyms are used on the Continent in a manner quite different from their English acceptation. With us biology is the total including morphology, physiology, embryology, and taxonomy. In France and Germany biology has a very indefinite meaning; bordering upon physiology.

Pharmacopœia, the equivalents of customary and metric weights and measures, and a table of thermometric equivalents, all from the same source.

It will be seen that in America, as in Germany, the nomenclature of chemical compounds for medical and pharmaceutical purposes differs greatly from that of commerce and of chemical science. Still the United States terminology is less perplexing than that recognised in the German empire. The American gallon is decidedly different from that used in Britain, being much smaller, equal in fact to the old English wine gallon. In weights, as used in the United States and in Britain, we can find no difference.

There are no comparative tables of the different hydrometric scales.

## CORRESPONDENCE.

### INSTRUCTION IN BACTERIOLOGY.

*To the Editor of the Chemical News.*

Sir,—I beg to call your attention to the evening classes in bacteriology held here. Two courses are given; the one (Course A) deals for the most part with the disease germs, the other (Course B) with the organisms of fermentation; and both courses form a good introduction to microscopy and bacteriology.

Bacteriology is daily becoming more important in its relation to chemical science, and many chemists might like to know of our courses.—I am, &c.,

R. T. Hewlett.

Bacteriological Laboratory,
King's College, W.C.

### INTERNATIONAL INDEX TO CHEMICAL LITERATURE.

*To the Editor of the Chemical News.*

Sir,—The publication in the Chemical News of October 20 of my Address to the Congress of Chemists at Chicago, on an "International Index to Chemical Literature," has brought me a letter from Dr. Bechhold, of Frankfurt-am-Main, in which he announces the speedy issue of a monthly index.

The material will be classified under sixteen principal headings and a number of minor ones, to wit:—

I. Apparatus.
II. Theoretical Chemistry:—(*a*) Gases. (*b*) Liquids. (*c*) Solids. (*d*) Solutions. (*e*) Atomic and Molecular Properties. (*f*) Affinities. (*g*) Thermo chemistry, (*h*) Electro-chemistry. (*i*) Photo chemistry and Spectroscopy. (*k*) Crystallography.
III. Inorganic Chemistry (arranged on the Periodic System).
IV. Organic Chemistry (arranged practically as in Beilstein's work).
V. Analytical Chemistry:—(*a*) General Methods. (*b*) Inorganic Substances. (*c*) Organic Substances. (*d*) Special Methods of Analysis; Sanitary, Physiological, and Legal Chemistry.
VI. Technical Chemistry (in forty sub-divisions).
VII. Physiological Chemistry (in twenty-three subdivisions).
VIII. Pharmaceutical Chemistry:—(*a*) New Remedies. (*b*) Valuations. (*c*) Galenical Preparations.
IX. Foods and Food Chemistry (in eighteen subdivisions).
X. Agricultural Chemistry:—(*a*) Soils. (*b*) Plant-culture. (*c*) Animal-feeding.
XI. Mineralogy.
XII. Bacteriology and Hygiene.
XIII. Official Reports and Laws.
XIV. Personal Notices and Biography.
XV. Statistics and Commerial Items.
XVI. Books.

This monthly index is intended to include all languages, and at the end of one year a year-index and at the end of ten years a general-index are planned. The work will be edited by Dr. Ephraim, and published by Bechhold, of Frankfurt-am-Main. The first number will be awaited with great interest, and chemists can but hope that the undertaking will completely fill the gap so long open, and so greatly needing to be closed.—I am, &c.,

H. Carrington Bolton.

University Club, New York City,
December 12, 1893.

**Institute of Chemistry Examinations.**—Of the candidates examined in the new Laboratories of the Institute at 30, Bloomsbury Square, the following have passed (11):—E. A. Andrews, Mason College, Birmingham; G. E. Brown, Mason College; R. M. Caven, University College, Nottingham; R. P. Charles, King's College, London; P. H. Kirkaldy, King's; C. A. Mitchell, King's; H. B. Stocks, University College, Liverpool; H. Tate, Royal University, Ireland; W. H. Willcox, University College, Notts.; S. B. Wright, student under E. G. Clayton, F.I.C., and at King's College; and H. S. Young, King's. Of candidates examined in Dublin the following five were successful, viz.:—W. S. Barratt, T. Byrne, P. M. Davies, H. E. Ivatts, and C. McMullen, all trained at the Royal College of Science, Dublin. Of candidates examined in Glasgow the following six were successful:—T. Chambers, Yorkshire College, Leeds, and Glasgow and West of Scotland Technical College; H. Findlay, R. Fulton, jun., W. Hannah, F. W. McKillop, each of Glasgow and West of Scotland Technical College, and N. McCulloch, Glasgow.

**The Analysis of Silicon Carbide.**—Dr. Otto Muhlhaeuser.—Carborundum is a grinding agent which is in part superseding bort and corundum. The difficulty in its analysis is its extreme hardness. Carborundum can only be brought into a state susceptible of being opened up by prolonged grinding in the agate mortar followed by elutriation with distilled water. The powder is shaken up with distilled water, allowed to subside for a given time, and the matter remaining in suspension after five minutes is submitted to analysis. The combustion of the carbide is effected in contact with lead chromate *alone*. For estimating the silicon the material is fused with a mixture of soda and potash.—*Zeitschrift f. Anal. Chem.*, xxxii., Part 5.

**On Borax as a Basis for Alkalimetry.**—Th. Salzer.—From the author's experiments it appears that accurate titration may be effected with a decinormal solution of borax, using litmus as indicator. The acid to be determined must be decinormal. It is coloured a faint onion-red with a *few* drops of sensitive tincture of litmus, and the solution of borax is added until the colour changes to a bluish-red and does not revert to onion-red. If the solution of borax is added until a pure blue colour is produced the value obtained is too high by about 10 per cent. Methyl-orange is preferable as an indicator only in the case of concentrated inorganic acid. For dilute acids it is less suitable, and for organic acids it is quite useless. Citric acid is preferably determined with potassa, using phenol-phthaleine as indicator.—*Zeitschrift f. Anal. Chem.*, xxxii., Part 5.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxvii., No. 24, December 11, 1893.

**The Sublimation of the Yellow and Red Mercury Iodides.**—M. Berthelot.—Mercuric iodide appears in two distinct isomeric conditions—as red iodide, stable at ordinary temperatures, and as yellow iodide, produced by the action of heat upon the former and stable at a high temperature. Both are crystalline. The yellow iodide can be easily converted into the red form at common temperatures, especially on contact with the least trace of crystals of the red iodide. This transformation, produced without the concurrence of any external energy, is intelligible because it is accompanied by a liberation of heat equal to + 3·0 cals. for $HgI_2 = 354$ grms. It is known that each of the iodides may be separated as such by the action of certain solvents at the ordinary temperature; the red iodide being in general obtained by precipitation (?), and the yellow form separating on cooling or by the addition of water to its alcoholic solution. Frankenstein considered that these two iodides might both exist in the state of isomeric vapours, on the faith of the following experiment. If we carefully heat a mixture of the two iodides upon a plate of glass, holding a second glass plate at a very small distance, and operating at a very low temperature so that the red crystals may not be transformed, there condenses upon the upper plate a sublimate containing at once yellow and red crystals. The experiment may be easily repeated, but it does not prove the existence of the two isomers in the state of vapour. Without doubt the condensation of the vapour of the mercuric iodide gives direct rise to the yellow iodide, but the contact of the least trace of crystals of the red iodide is sufficient to change the yellow iodide to the red form. But if we examine the conditions of the above experiment it is easy to recognise the impossibility of avoiding the projection of fine dust of the red iodide, placed upon the lower plate, which deprives the conclusion of all validity.

**Transformation Produced in Iron by a Permanent Deformation in the Cold.**—Georges Charpy.—It appears that a permanent deformation in the cold produced in irons and steels of different kinds a modification which may be regarded, at least provisionally, as an allotropic transformation of iron, the two states produced being called by Osmond iron $\alpha$ and iron $\beta$.

**Rates of Etherification of Hydrofluoric Acid.**—Maurice Meslans.—The rate of etherification decreases rapidly when the proportion of water accompanying the hydrofluoric acid increases, but etherification takes place even with the acid mixed with 2 vols. of water, but at the temperature of 220°, at which this hydrate must be strongly dissociated.

**Analysis of the Butters of Commerce.**—C. Violette.—(See p. 312).

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 4, Vol. viii., No. 93.

**On Alloys.**—Prof. W. C. Roberts-Austen.—This paper is the translation of the Second Report given in by the author to the Alloys Research Committee of the Institute of Mechanical Engineers.

**Liquid Chlorine.**—M. Fribourg.—From the *Bull. de la Soc. Chim. de Paris.*

## MEETINGS FOR THE WEEK.

Tuesday, Jan. 2nd.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.
—— Pathological, 8.30.
Thursday, 4th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.
Friday, 5th.—Quekett Club, 8.
—— Geologists' Association, 8.
Saturday, 6th.—Royal Institution, 3. "Air, Gaseous and Liquid," by Prof. Dewar, M.A., LL.D., F.R.S.

## TO CORRESPONDENTS.

*R. W. Rose.*—The rules you send are well known. Those recently printed are supposed to be simpler.

# INDEX.

END OF VOLUME LXVIII.